JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Quantitative Determination of PAHs in Biochar: A Prerequisite To Ensure Its Quality and Safe Application

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Supporting Information

ABSTRACT: Biochar is increasingly promoted as a beneficial soil conditioner. However, it may contain residues of polycyclic aromatic hydrocarbons (PAHs) as a result of its production by pyrolysis. To date, analytical methods to analyze PAHs in biochar quantitatively are hardly available. This study presents an optimized and validated procedure to quantify the 16 U.S. EPA PAHs in biochar. PAHs were best extracted with Soxhlet for 36 h using 100% toluene. Average absolute recoveries of isotope labeled internal standards used for each analyte from three different biochars ranged from 42% to 72%, and relative recoveries were between 71% and 105%. The limits of detection were biochar-dependent, but on average a factor of >50 lower than quantified PAH concentrations (9−355 mg $kg_{dry\ weight}^{-1}$). The established method prepares the ground for a harmonized protocol for PAH analysis of biochars, a necessity for biochar quality control, registration, and legislation.

KEYWORDS: *biochar, charcoal, polycyclic aromatic hydrocarbons, total concentrations, extraction method*

INTRODUCTION

Biochar is charcoal produced by pyrolysis of biomass and used as a soil conditioner with a view to sequester carbon and concurrently improve soil functions.[1,2] While there are a series of positive effects associated with biochar soil amendment (e.g., increased microbial biomass and microbial activity, increased plant production, liming effect, enhanced sorption capacity for organic contaminants), there are still many unknowns (e.g., with regard to carbon negativity, influence on nutrient cycles and availabilities, soil−water household), and even negative aspects have been stated (e.g., crop residue removal for, and occupational health and fire hazards during, biochar production).[2] Among the latter ones, the risk to contaminate soils seems inherent, as biochar may contain considerable amounts of polycyclic aromatic hydrocarbons (PAHs), as indicated by several reports of PAH residues in biochar-related combustion/pyrolysis materials. For instance, Brown et al.[3] quantified concentrations from 3 to 28 mg kg^{-1} in synthetic wood char (sum of 40 individual PAHs), Jonker and Koelmans[4] reported a charcoal to contain 45 mg kg^{-1} PAHs (sum of 13 individual compounds), and Schimmelpfennig and Glaser[5] found mean concentrations that ranged from 3.9 (Pyreg) to 2945 mg kg^{-1} (wood gasifier). Apart from this, the content of PAHs in biochar has hardly been investigated systematically, and neither have measures for their minimization during biochar production. Moreover, methods specifically adapted and validated for PAH analysis in biochar are hardly available. Previously used generic methods describing total PAH extraction from biochar are, e.g., found in Singh et al.[6] who determined "negligible" concentrations of <0.5 mg kg^{-1} PAHs, and concluded that these low levels "make these biochars safe for soil application". However, Singh et al.[6] used a 12 h Soxhlet extraction with dichloromethane, which may not be the ideal extraction solvent, as Fernandes and Brooks[7] stated that samples (i.e., straw and wood charcoal, vegetation fire residues, and chimney soot) "extracted with dichloromethane, or a mixture of dichloromethane and methanol, showed low recoveries of PAH internal standards. To overcome this problem, hexane was used as the extraction solvent." Schimmelpfennig and Glaser[5] used an 8 h Soxhlet extraction with hexane, a generic method by the German TÜV, to quantify PAHs in differently produced biochars. Gomez-Eyles et al.[8] quantified PAH in biochar at only 1.2 mg kg^{-1} using acetone/hexane (1:1). Brown et al.[3] used an analytical method with either toluene/methanol (1:1) or dichloromethane established earlier by Poster et al.[9] for Diesel soot. Overall, the analytical methods used thus far for PAH determination in biochar, or biochar related materials, are highly divergent. In light of the above, several official methods commonly applied by private laboratories (e.g., ISO 38 414 using cyclohexane, DIN EN 15527 using petroleum ether) may also fall short to determine PAHs in biochar quantitatively. This would have consequences for the optimization of biochar quality and quality control, is problematic from the point of view of biochar registration and legislation, and may lead to unnecessary and uncontrolled high PAH exposure in biochar recipient matrices.

The aim of this study is therefore to provide an easy and validated method to quantitatively extract the 16 PAHs defined by the U.S. EPA from biochar for researchers, practitioners, and legislators. The method was optimized with regard to solvent composition, extraction technique and duration, and extract cleanup, using a series of different representative biochar samples. As a starting point, toluene was used because (1) DIN ISO13877 states that highly contaminated soils are best extracted with toluene, and (2) Jonker and Koelmans[4] got

Received: December 22, 2011
Revised: March 7, 2012
Accepted: March 7, 2012
Published: March 7, 2012

Table 1. Properties of the Biochars Used for the Method Development and Concentrations of the 16 EPA PAHs Obtained with the Optimized Analytical Method (See Text)[a]

feedstock	unit	biochar 1 grapevine wood, 1 year old	biochar 2 *Miscanthus* (elephant grass)	biochar 3 sieved coniferous wood residues	biochar 4 sieved deciduous and coniferous residues
max pyrolysis temperature	[°C]	600	750	750	750
C	[%]	79.9	80.0	76.7	67.8
H	[%]	3.1	0.5	0.6	1.1
O	[%]	12.9	2.3	6.2	8.3
H/C (atom)		0.47	0.08	0.10	0.20
O/C (atom)		0.12	0.02	0.06	0.09
surface area	[$m^2\ g^{-1}$]	6.8	362	123	226
no. of analysis		$n = 2$	$n = 21$	$n = 9$	$n = 11$
NAP	[$\mu g\ kg_{dw}^{-1}$]	5941 (125)	26 089 (2779)	181 160 (29 134)	5143 (249)
ACY	[$\mu g\ kg_{dw}^{-1}$]	38 (12)	5495 (671)	38 730 (1046)	367 (158)
ANA	[$\mu g\ kg_{dw}^{-1}$]	109 (10)	498 (457)	1699 (766)	189 (159)
FLU	[$\mu g\ kg_{dw}^{-1}$]	611 (26)	256 (330)	987 (761)	89 (10)
PHE	[$\mu g\ kg_{dw}^{-1}$]	1760 (80)	9509 (765)	48 836 (1689)	1605 (83)
ANT	[$\mu g\ kg_{dw}^{-1}$]	419 (12)	1772 (245)	9774 (431)	330 (17)
FLT	[$\mu g\ kg_{dw}^{-1}$]	217 (22)	6628 (808)	31 527 (872)	433 (25)
PYR	[$\mu g\ kg_{dw}^{-1}$]	252 (27)	5869 (577)	22 458 (635)	355 (22)
BaA	[$\mu g\ kg_{dw}^{-1}$]	141 (16)	940 (161)	4416 (213)	134 (25)
CHR	[$\mu g\ kg_{dw}^{-1}$]	151 (25)	1062 (184)	4811 (362)	169 (31)
BbF	[$\mu g\ kg_{dw}^{-1}$]	22 (2)	856 (335)	3600 (244)	75 (42)
BkF	[$\mu g\ kg_{dw}^{-1}$]	35 (4)	456 (243)	2105 (203)	53 (51)
BaP	[$\mu g\ kg_{dw}^{-1}$]	61 (5)	1432 (649)	4711 (498)	64 (29)
IPY	[$\mu g\ kg_{dw}^{-1}$]	37 (0)	690 (455)	3152 (211)	42 (31)
DBA	[$\mu g\ kg_{dw}^{-1}$]	1 (0.3)	51 (36)	238 (27)	2 (3)
BPE	[$\mu g\ kg_{dw}^{-1}$]	21 (1)	1128 (501)	2821 (108)	44 (26)
∑16 EPA PAH	[$\mu g\ kg_{dw}^{-1}$]	9818 (116)	62 732 (5938)	355 295 (30902)	9113 (454)

[a]Numbers in parentheses indicate standard deviations of *n* replicates. PAHs are naphthalene (NAP), acenaphthylene (ACY), 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 the 16 EPA PAHs (Σ16 EPA PAHs).

best results with toluene for their charcoal. Validation encompasses figures of merit such as absolute and relative recoveries, precision, and method detection limits. Finally, the relevance of the obtained quantitative results is discussed from the point of view of biochar quality, legislation, and soil protection.

MATERIALS AND METHODS

Chemicals and Materials. A mixture containing each of the 16 EPA PAHs [i.e., 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)] at 100 ± 1 $\mu g\ mL^{-1}$ toluene was purchased from Promochem (Wesel, Germany). Individual solutions at 200 ± 20 $\mu g\ mL^{-1}$ isooctane or toluene of the following deuterated PAH were obtained from Cambridge Isotope Laboratories (Andover, MA): 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. Indeno[1,2,3-*cd*]fluoranthene (IFL; 99.7% purity) was received in solid form from Promochem (Wesel, Germany).

Cyclohexane, dichloromethane, toluene, ethanol, isooctane (all Suprasolv for gas chromatography), and *N*,*N*-dimethylformamide (Suprasolv, for organic trace analysis) were purchased from Merck (Darmstadt, Germany). Hexane (96%, for pesticide residue analysis) and 2-propanol were provided from Scharlau (Barcelona, Spain). Deionized water was further treated with a milli-Q Gradient A10 water purification system (Millipore, Billerica, MS). Helium and nitrogen gas 5.0 and 4.0, respectively, were from Pangas (Dagmarsellen, Switzerland). Sodium sulfate (pro analysi) and silica gel 60 (0.063−0.200 mm) for column chromatography was obtained from Merck (Darmstadt, Germany). Silanized glass wool for cleanup columns was purchased from Macherey & Nagel (Düren, Germany), and Soxhlet extraction thimbles 30 × 80 mm were from Whatman (Maidstone, England). Hydromatrix was purchased from Separtis (Grenzach-Wyhlen, Germany), and silicon dioxide (sand) acid washed and calcined (puriss. p.a.) was from Riedel-de Haën (Seelze, Germany).

Biochars. Four different biochars (Table 1) of commonly used feedstock were used for method development and validation. They were selected because they represent important and abundant biowaste types. All the biochars investigated here were produced by pyrolysis where the feedstock is thermochemically decomposed at a temperature range from 350 °C (start of combustion) to 750 °C (max. combustion temperature) in an oxygen-poor atmosphere (1−2% O_2). Biochar 1 (SI Figure S1) was provided by Torres winery (Vilafranca, Spain), and biochar 2 (SI Figure S2) and biochar 3 (SI Figure S3) were obtained from Pyreg GmbH (Doerth, Germany). Biochar 4 (SI Figure S4) was from Swiss Biochar GmbH (Belmont-sur-Lausanne, Switzerland). Biochar 1 was produced of vine wood, biochar 2 was produced of elephant grass (*miscanthus*), and biochar 3 and biochar 4 were pyrolyzed from coniferous wood, and coniferous and deciduous residues, respectively (Table 1).

For characterization of the biochars, C- and H-contents were measured after dry oxidation. Oxygen was measured after pyrolysis of the sample at 1000 °C and reduction to carbonoxide. All elements were measured with a Euro EA apparatus, HEKAtech GmbH (Wegberg, Germany). The specific surface area was determined by nitrogen adsorption and Brunauer−Emmett−Teller (BET) isotherm

with a NOVA 2e from Quantachrome Instruments (Odelzhausen, Germany).

Sample Preparation and Extraction. All biochars were first dried at 40 °C overnight and then ground to 0.75 mm with a cutting mill SM1 Retsch GmbH (Haan, Germany). Additionally, some of the ground biochars were sieved at 0.25 mm, and others were ball milled also from the 0.75 mm fraction. All biochars were stored in amber glass at a dry place and at room temperature. Prior to extractions, samples were thoroughly mixed with a Turbula shaker-mixer Bachofen AG (Muttenz, Switzerland). An aliquot of the samples was put in the oven at 105 °C for 4 h in order to determine the dry weight of the biochars.

For the method development with Soxhlet extraction, different solvents and extraction durations were tested. Toluene 100% was used as a starting solvent[4] and compared with several mixtures, i.e., toluene/methanol (1:6, v/v; best suited for wood soot, according to ref 4), dichloromethane/acetone (1:1, v/v; recommended solvent in the Dionex application note, see below), toluene/ethanol (2:1, v/v), toluene/propanol (2:1, v/v), toluene/hexane (2:1, v/v), toluene/heptane (2:1, v/v), and toluene/dichloromethane (2:1, v/v). Hexane (100%) used by Fernandes and Brooks[7] and heptane (100%) were also tested as alternative extraction solvents. Extractions were run for 15 or 36 h, and the sample size was 1 or 0.1 g (see below).

Soxhlet extraction was compared with accelerated solvent extraction using an accelerated solvent extractor (ASE 200) from Dionex GmbH (Idstein, Germany). The 11 mL ASE cells were half filled with hydromatrix. Then, 1 g of biochar was filled into the cell, and the rest of the space was filled with hydromatrix. The extraction program was based on the ASE Dionex application note 313 for PAHs in soil and sediment. Therein, the extraction parameters are set as follows: temperature 100 °C, sample weight 1−10 g, pressure 2000 psi (13.79 MPa), preheating 5 min, static (extraction) time 5 min, extraction solvent dichloromethane/acetone (1:1, v/v), flush volume 60%, purge time with nitrogen gas 1 MPa for 60 s. Additionally, a pressure of 1500 psi was also tested as well as toluene 100%, and toluene/methanol (1:6, v/v). Further, static cycles were done twice. Total extraction time of one sample was 20 min, and the extract volume was approximately 22 mL.

Sample Cleanup. Sample cleanup of PAH was performed according to Bucheli et al.[10] Briefly, the Soxhlet extracts, to each of which 1 mL of isooctane was added as a keeper, were concentrated with a Syncore Analyst system from Büchi (Flawil, Switzerland) and cleaned by dimethylformamide/Milli-Q water (9:1, v/v) liquid−liquid partitioning and over 10%-water-deactivated silica gel. In contrast to the referenced method, where a 25% aliquot of the concentrated extract was taken, all of the 1 mL concentrate was used for the cleanup. To test the robustness of the method, the second or both of the described cleanup steps were omitted, and the influence of the extract cleanness on the quantification was assessed.

PAHs Separation and Determination by GC-MS. Analysis of PAH was conducted as described in Bucheli et al.[10] Briefly, the PAHs were separated on an Agilent GC 6890N by on-column injection of 1 μL of the extract. Separation was performed on a Rtx-5Sil MS capillary column (30 m, 0.25 mm internal diameter (i.d.), 0.25 μm film thickness) from Restek (Bellefonte, PA). As a retention gap, a 2 m Siltek guard column (0.53 mm i.d.) from the same provider was mounted before the separation column. Helium was used as a carrier gas at a constant flow of 1 mL min^{-1}. The injector temperature was set to oven track mode (3 °C above oven temperature at all times), and the oven temperature was programmed as follows: 1 min at 100 °C, to 300 at 5 °C min^{-1}, and 15 min at 300 °C. Detection was performed with an Agilent MS 5973i in the electron impact mode with a 70 eV ionization energy and single ion monitoring. Identification of a given analyte was assured by using two compound-specific ions with a mass ratio similar to the one determined with internal calibration. For all PAHs (including IFL) and all deuterated internal standards, the quantifier ion corresponded to the respective molecular weight (m/z = $M^{+\cdot}$), and the qualifier ion was $[M - 2H]^+$ for all PAHs and $[M - 2D]^+$ for internal standards. Quantification was carried out using the internal standard method. Toluene mixtures containing different amounts of analytes (7.5−2500 pg μL^{-1}) and constant amounts of internal (and recovery) standards (200 pg μL^{-1}) were used for calibration.

Method Validation. Analytical figures of merit determined for each of the 16 EPA PAH were absolute and relative recoveries, method precision, limits of detection (LoD), blank concentrations, and linearity. Absolute recoveries (also known as surrogate recoveries; in percent) were routinely quantified by relating the deuterated internal standards (surrogate standards) added before extraction to the recovery standard (IFL) added before sample analysis, in comparison to the same ratio in the calibration solvents. The absolute recovery delineates the analyte losses during the preparation from analyte losses during separation/detection. To determine relative recoveries (spike recoveries), 1000 or 2000 μg kg^{-1} of each individual PAH were spiked to the biochars before extraction. Recoveries were obtained by dividing the quantified minus the native amount (both determined with the internal standard method) of each analyte by its added amount and are also given in percent. The relative recoveries mirror the suitability of the deuterated internal standards to compensate for analyte losses during analysis and depict the robustness of the analytical procedure. Recovery analyses were carried out in triplicates. Precision was obtained as the relative standard deviation of concentrations obtained with three and four replicate analyses of native biochars 4, and 2 and 3, respectively. The LoD was obtained from the very same chromatograms as the average of three times the noise times the concentration divided by the respective signal. The limit of quantification (LoQ) was obtained similarly, but with a factor of 10 instead of 3. The blank concentrations were determined as the average of nine empty thimble runs throughout the method development process. The results were not blank corrected.

Statistics. Mean and standard deviation of usually three to four replicates were used to compare results of different analytical figures of merit. Student t tests were conducted to evaluate different method optimization steps with Excel (2007) by comparing the concentrations of each of the 16 EPA PAHs and the Σ16 EPA PAHs obtained with the different solvent mixtures, with Soxhlet and ASE, with 15 and 36 h extraction duration, and with 0.1 g with 1 g sample weight. An analysis of variance (ANOVA) was applied to evaluate the cleanup steps with R version 2.13.2 (2011−09−30).

RESULTS AND DISCUSSION

Representativeness of Biochars Used for Method Development and Validation. Table 1 presents the properties of biochars 1−4 such as feedstock type, C-, H-, and O-elemental concentrations, and specific surface areas. Properties of biochars can vary widely depending on feedstock and production process. According to Kookana et al.[11] the H/C and O/C ratios can narrow with increasing condensation. The biochars for the method development had H/C atomic ratios of 0.1−0.5 and O/C atomic ratios of 0.02−0.12 (Table 1). They are well within the range of biochars reviewed by Kookana et al.[11] According to Lehmann and Joseph[1] the specific surface area of biochars depends on activation time and temperature. Typically, biochars from fast pyrolysis have rather low surface areas such as <8 m^2 g^{-1} for switchgrass.[12] Biochar 1 was noticeably different than biochars 2−4 with regard to its specific surface area (7, as opposed to 123−362 m^2 g^{-1}, Table 1) and seemed to be produced by fast pyrolysis. In this respect, it resembled wood or coal soot, for which similarly low specific surface areas were reported.[13] The other biochars with high specific surface areas in the hundreds of m^2 g^{-1} were comparable to such heated to >500 °C.[11] However, biochars 2−4 had substantially lower specific surface areas than activated charcoal, which are mostly around or even higher than 1000 m^2 g^{-1}.[14] Thus, while the individual properties of four selected biochars spread widely within the ranges typical for biochars, they seemed to be representative for this kind of material

overall, which legitimates their use for the method development.

Method Optimization. *Solvent Tests with Soxhlet Extraction.* As a starting point toluene was used because it showed the best recovery results for charcoal.[4] With toluene mixtures, other extraction solvents were tested systematically. Figure 1A depicts concentrations extracted from biochar 2 with toluene/methanol (1:6, v/v) and dichloromethane/acetone (1:1, v/v) relative to those with toluene 100%. The toluene/methanol solvent mixture represents the best extraction solvents for traffic, oil, coal, and wood soots according to Jonker and Koelmans.[4] The dichloromethane/acetone mixture is the recommended extraction blend for sediments and soils according to the Dionex application note 313. The 2:1 (v/v) blends of a variety of solvents with toluene are shown in Figure 1B.

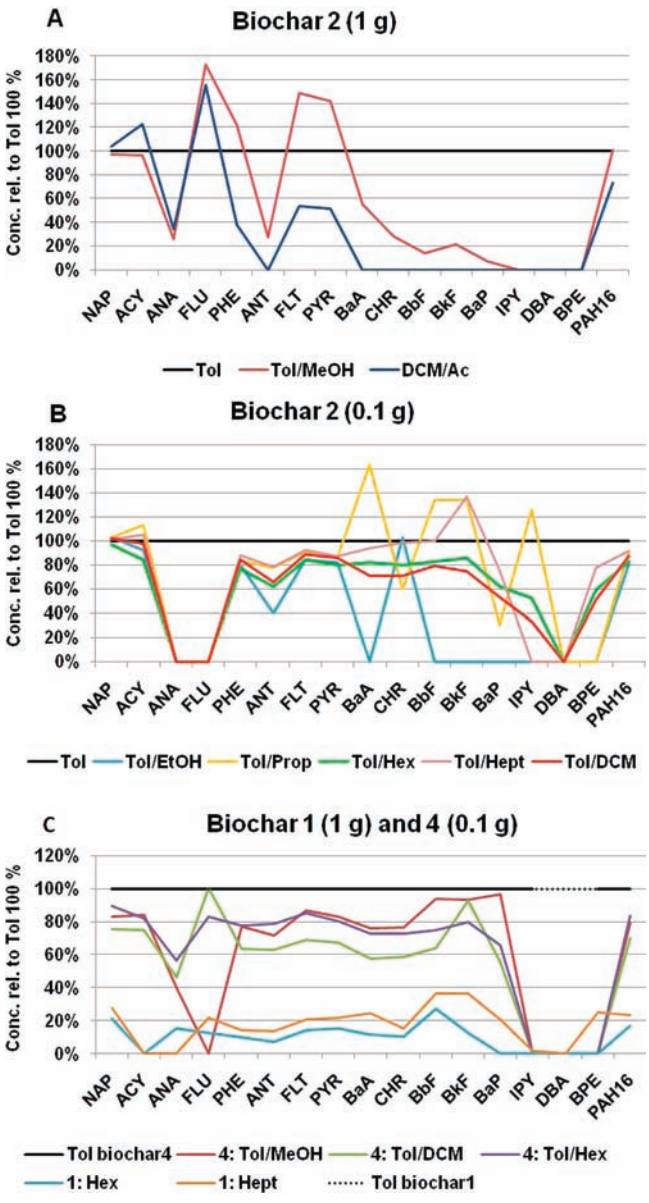

Figure 1. Soxhlet extractions of 1 g of biochar 2 (panel A), 0.1 g of biochar 2 (panel B), 1 g of biochar 1, and 0.1 g of biochar 4 (panel C) for 36 h with toluene (Tol) 100% as reference extraction solvent (black line at 100%) in comparison to toluene/methanol (Tol/MeOH; 1:6, v/v) and dichloromethane/acetone (DCM/Ac; 1:1, v/v) (panel A), to toluene/ethanol (Tol/EtOH; 2:1, v/v), toluene/propanol (Tol/Prop; 2:1, v/v), toluene/hexane (Tol/Hex; 2:1, v/v), toluene/heptane (Tol/Hept; 2:1, v/v), and toluene/dichloromethane (Tol/DCM; 2:1, v/v) (panel B), and to Hex 100% and Hept 100% (biochar 1), and Tol/MeOH (1:6, v/v), Tol/DCM (2:1, v/v), and Tol/Hex (2:1, v/v) (biochar 4) (panel C). Biochar 4 did not contain DBA (panel C, interrupted black line) in contrast to biochar 1 (panel C, dotted black line). For PAH abbreviations, see text.

Generally, none of the solvent combinations extracted more PAHs ($\sum$16 EPA PAH) from biochar 2 than toluene (Figure 1A,B). The differences were not larger than 30% for Σ16 EPA PAH, though, and statistically not significant (SI Table S1, *t* tests results also indicated for individual PAH compounds), because NAP, the prevailing compound, was mostly well extracted. However, PAHs with four or more rings were either not (e.g., dichloromethane/acetone; Figure 1A), only poorly (e.g., toluene/dichloromethane; Figure 1B), or inconsistently (toluene/propanol; Figure 1B) extracted by solvents other than toluene. The same picture of absent or inconsistent extraction capability was observed for all tested solvent compositions in comparison to toluene, even for some of the light PAHs, i.e., ANA and FLU.

Further tests were run with biochars 1 and 4 and more solvent mixtures (Figure 1C, SI Table S2) to consolidate the findings so far. Both biochars were chosen because they represent different feedstocks, and contained about 6 times less PAHs than biochar 2 (Table 1). Again, all solvents extracted less PAHs than toluene (20% < Σ16 EPA PAHs < 80%, relative to toluene). Solvent mixtures containing toluene/methanol, toluene/dichloromethane, and toluene/hexane (2:1, v/v each) performed better than the pure solvents hexane and heptane, but some heavy PAHs were always absent.

Thus, the best solvent to extract PAHs from biochars seemed to be toluene. This result is not surprising considering the cohesive properties and solubilities of PAHs. As a rule of thumb, structural similarity favors solubility.[15] Generally, the cohesive energy of a molecule is a linear combination of the hydrogen bonding, the dispersion coefficient, and the polarity and is added up in the Hildebrand solubility parameters (see SI).[15] For each of the 16 EPA PAHs, the dispersion coefficient contributed to almost a 100% to the cohesive energy. Of all the solvents used in this study, toluene has the highest dispersion coefficient and its linear combination of cohesive forces matches best with those of the PAHs.

Other researchers[16] also used best solvent's prediction tools such as the Hildebrand solubility parameters to learn about the optimal extraction solvent for organic compounds. Yet the predicted optimal solvents did often not perform best in practice, because Hildebrand parameters do not consider the influence of and interactions with the matrix and the analytes.[16] For instance, Brandli et al.[17] found dichloromethane 100% and hexane/acetone (1:3, v/v) to better extract PAHs from compost than toluene, for which absolute recoveries were only around 30%. Obviously, these solvents were more capable of interacting with compost, and acetone in particular is often used as a mediating solvent between rather unpolar solvents and more polar matrices.[17] As biochars mainly consist of highly condensed aromatic structures similar to toluene, this extraction solvent seems ideally suited both from the point of view of the analyte, and the sample matrix.

Extraction Time with Soxhlet. After toluene was identified as the best extraction solvent, the extraction time needed to be optimized as well. Therefore, 36 h of Soxhlet extractions of

dx.doi.org/10.1021/jf205278v | J. Agric. Food Chem. 2012, 60, 3042−3050

Table 2. Analytical Figures of Merit for Quantification of 16 EPA PAHs in Biochars 2−4[a]

	biochar 2				biochar 3				biochar 4				
	abs [%]	rel [%]	prec [%]	LoD [μg kg_{dw}^{-1}]	abs [%]	rel [%]	prec [%]	LoD [μg kg_{dw}^{-1}]	abs [%]	rel [%]	prec [%]	LoD [μg kg_{dw}^{-1}]	blank concs [μg kg_{dw}^{-1}]
no. of replicates	3	3	4	4	3	3	4	4	3	3	3	3	9
spike conc [μg kg_{dw}^{-1}]		1000				2000				1000			
NAP	35 (7)	48 (3)	14	838 (225)	53 (2)	112 (25)	10	3021 (643)	36 (3)	164 (31)	4	41 (41)	425 (278)
ACY	23 (4)	69 (6)	16	53 (12)	45 (6)	88 (14)	3	446 (124)	17 (9)	97 (13)	7	9 (2)	7 (6)
ANA	38 (5)	82 (16)	61	32 (22)	57 (12)	85 (22)	67	17 (5)	40 (4)	120 (36)	26	4 (1)	29 (20)
FLU	35 (4)	48 (9)	48	18 (6)	47 (6)	65 (17)	141	16 (8)	37 (8)	50 (10)	2	6 (2)	30 (32)
PHE	55 (9)	79 (8)	10	48 (8)	75 (15)	94 (16)	3	1432 (2303)	55 (11)	95 (3)	2	7 (2)	36 (27)
ANT	50 (8)	80 (9)	10	50 (22)	73 (15)	94 (17)	4	268 (123)	46 (15)	103 (5)	5	36 (22)	8 (9)
FLT	56 (9)	81 (10)	8	33 (8)	77 (13)	107 (19)	4	434 (152)	60 (13)	103 (6)	6	5 (0)	8 (12)
PYR	55 (8)	74 (9)	8	30 (5)	76 (13)	90 (15)	4	187 (114)	58 (13)	96 (7)	2	4 (1)	9 (9)
BaA	57 (6)	85 (9)	4	14 (3)	80 (6)	98 (20)	6	60 (39)	56 (22)	108 (7)	5	2 (1)	n.d.
CHR	66 (9)	78 (11)	3	26 (6)	88 (12)	93 (17)	9	95 (28)	64 (15)	102 (6)	5	5 (2)	n.d.
BbF	76 (8)	60 (8)	3	11 (3)	95 (11)	70 (13)	7	32 (11)	55 (26)	82 (7)	15	2 (1)	n.d.
BkF	70 (8)	69 (8)	4	21 (5)	94 (9)	82 (16)	9	108 (20)	53 (28)	95 (11)	14	4 (2)	n.d.
BaP	39 (5)	69 (7)	6	64 (19)	60 (14)	83 (15)	8	157 (35)	28 (23)	103 (15)	26	6 (3)	n.d.
IPY	49 (5)	76 (8)	13	42 (19)	74 (7)	90 (20)	9	85 (40)	15 (9)	120 (28)	17	9 (4)	n.d.
DBA	64 (4)	66 (6)			83 (10)	77 (16)	4	56 (40)	33 (20)	106 (5)			n.d.
BPE	57 (4)	76 (6)	7	33 (12)	75 (8)	91 (19)	3	117 (66)	16 (8)	130 (26)	14	11 (6)	n.d.
16 EPA PAHs	52 (14)	71 (11)	12 (17)		72 (15)	89 (12)	7 (37)		42 (17)	105 (24)	4 (8)		

[a]Abs = absolute recovery; rel = relative recovery; prec = precision; LoD = limit of detection (3 × noise × concentration)/signal; n.d. = not detected. Numbers in parentheses indicate standard deviations of *n* replicates. PAHs are naphthalene (NAP), acenaphthylene (ACY), 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 the 16 EPA PAHs (Σ16 EPA PAHs).

dx.doi.org/10.1021/jf205278v | J. Agric. Food Chem. 2012, 60, 3042−3050

biochar 2 with toluene (Tables 1, 2) were compared with 15 h in terms of concentrations and absolute recoveries. While BkF, IPY, and DBA showed up to 3 times higher concentrations when extracted for 15 h only from biochar 2, the Σ16 EPA PAHs was 4% higher after 36 h. The differences were statistically significant only for NAP, ANA, and ANT (SI Table S3). More importantly, however, the absolute recoveries of the heavy deuterated PAHs (d_{12}-BbF−d_{12}-BPE) were drastically reduced after 15 h extraction only (10 ± 9%, as opposed to 59 ± 14% for 36 h, biochar 2, mean recovery of individual PAHs from BbF to BPE, Table 2), thus rendering the results of heavy PAHs stated above unreliable. We hypothesize that the deuterated internal standards, used for quality control reasons, were strongly sorbed to the biochar after spiking, thus requiring an extended period of time/number of Soxhlet cycles to be desorbed again.

Accelerated Solvent Extraction. An ASE was used with different solvents, and instrumental settings as in the Dionex application note 313 for PAH analysis in soils and sediments. The results from the ASE were compared with 36 h Soxhlet extractions using the same solvent compositions. Figure 2

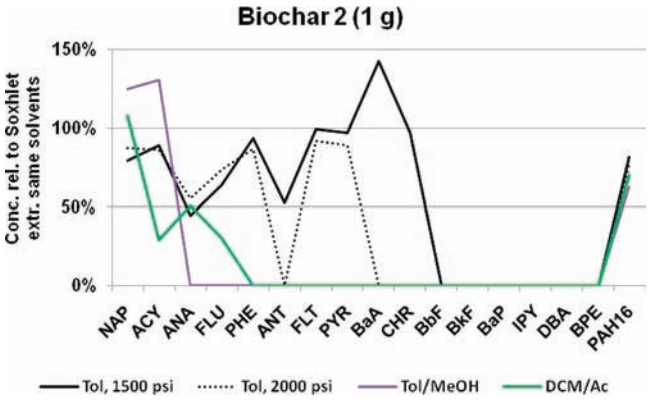

Figure 2. Results from accelerated solvent extraction with toluene (Tol) 100% at 1500 and 2000 psi and with toluene/methanol (Tol/MeOH; 1:6, v/v) and dichloromethane/acetone (DCM/Ac; 1:1, v/v). All concentrations are normalized to those obtained with 36 h Soxhlet extractions with the same respective solvent compositions.

depicts the ASE extracted concentrations relative to those obtained with Soxhlet extractions (for quantitative figures, see SI Table S4). The performance of ASE was consistently inferior to Soxhlet extraction (60% <Σ16 EPA PAHs <80%, relative to Soxhlet; Figure 2), irrespective of the solvent composition [toluene 100%, toluene/methanol (1:6, v/v), and dichloromethane/acetone (1:1, v/v)], and the ASE pressure (1500 or 2000 psi). In particular, ASE was not capable of extracting any of the PAHs heavier than CHR.

Extract Cleanup. The influence of different cleanup steps was tested as described above. The concentrations of the PAHs obtained with the different procedures, both as a sum and individually, were not significantly different (ANOVA p-value >0.05), except for BaP (p-value = 0.036) and DBA (p-value = 0.038) (Figure 3). For both compounds the DMF-only cleanup showed the least concentrations. Overall, given the only marginal or nonexisting differences in quantified concentrations, and the considerable reduction in work load, resources, and analysis time, particularly in view of the foreseen application of the method in practice, we consider omission of any extract cleanup both affordable and recommendable.

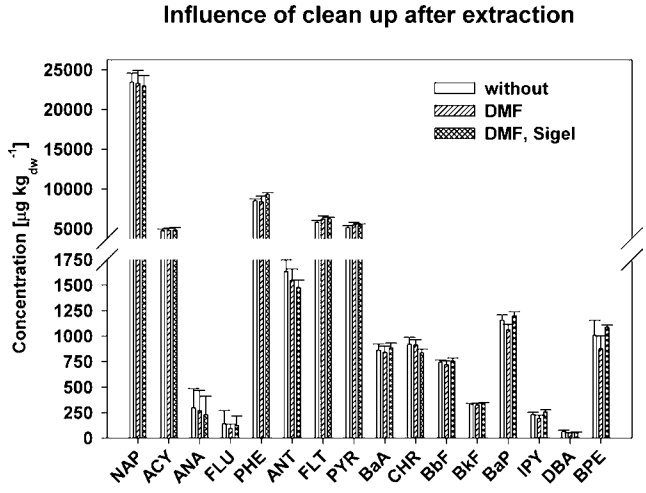

Figure 3. Influence of different cleanup steps applied to 36 h Soxhlet toluene extracts. Cleanup steps were liquid−liquid partitioning with *N*,*N*-dimethylformamide (DMF) alone or followed by elution over a silica gel (Sigel) column. Error bars depict one standard deviation of three replicates (*Y*-axis breaks from 1750 to 4500 μg kg_{dw}^{-1}).

In conclusion, the optimized method includes Soxhlet extraction for 36 h with 100% toluene and an extract concentration to 1 mL without any further cleanup.

Sample Representativeness. The extraordinary range of concentrations of individual PAHs observed in the four biochars used for method development posed a challenge for their concomitant analysis. NAP was the overall dominating PAH in all of the biochars investigated, with relative contributions of 42−61% of the Σ16 EPA PAHs and concentrations that were up to 5900 times higher than those of other individual PAHs (Table 1). This led to the situation that often the most concentrated PAH (NAP) fell outside of the linear range of the GC-MS. To account for such a disparate PAH concentration range under the given analytical prerequisites (e.g., the use of isotope labeled internal standards for all individual analytes in affordable amounts), we tested sample dilution. Subsamples of 1 g of biochar 2 or 4 were diluted with 9 g sodium sulfate, silica gel, or silicon dioxide and thoroughly mixed with a Turbula shaker-mixer overnight. Thereof, 1 g was analyzed for its PAH content (biochar 2, four replicates; biochar 4, two replicates), and the result was compared with the one obtained from the original material (biochar 2, two replicates; biochar 4, six replicates). A two sided, unpaired t test of the Σ16 EPA PAHs revealed no significant differences (p-values >0.05) between a biochar sample weight of 0.1 and 1 g. This indicates that dilution is an appropriate way to account for drastically elevated NAP concentrations, and that even small amounts of samples are still representative if they are carefully prepared in the described way. However, when only a tenth of the sample was used, some heavy PAHs such as DBA in biochar 2 and BaP, IPY, and DBA in biochar 4 (Table 1) fell below the LoD. In practice, this means that sometimes two analyses with varying amounts of biochar may be required to account for the occurrence of individual PAHs being present at widely varying concentrations.

Particle Size. The optimized method was applied to biochars with particle size of <0.75 mm. During the method development the influence of the particle size was also tested. Therefore, biochar 2 (<0.75 mm) was further sieved <0.25 mm, or ground with a ball mill. The sieve fraction <0.25 mm

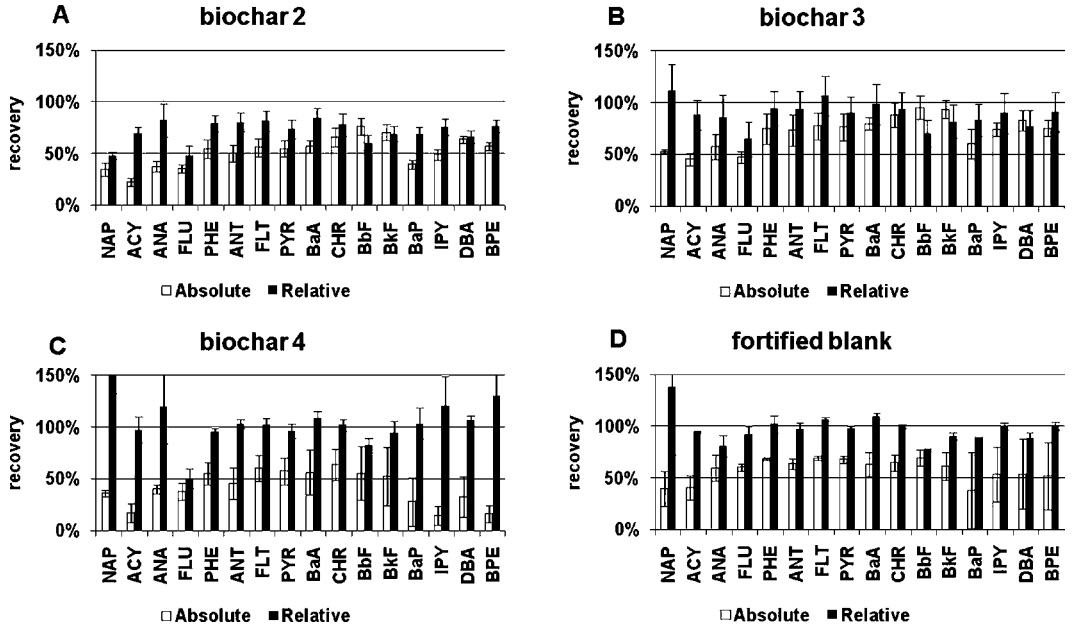

Figure 4. Absolute, and relative, recoveries, of deuterated internal standards, and of 1000 or 2000 (biochar 3) μg kg^{-1} 16 EPA PAHs, respectively, from biochar 2 (panel A), biochar 3 (panel B), biochar 4 (panel C), and from a method blank (panel D).

had a 40% higher Σ16 EPA PAH content than the extracts from the <0.75 mm fraction. As most (extractable) PAHs probably resided on surfaces, a change in surface to volume (mass) ratio would inherently lead to different mass based concentrations. In other words a dilution effect was probably observed in the more bulky <0.75 mm fraction. In contrast, the ball mill treated biochars had the same Σ16 EPA PAH concentration as the one sieved to <0.75 mm, indicating that PAHs residing on, and in, particles of such a size range were efficiently extracted with the optimized method. Hence, the sample preparation (ground to <0.75 mm) and sample amounts (1 g) used for this method led to representative samples and reproducible PAH quantification.

Method Validation. Linearity with R^2 > 0.99 throughout the whole optimization procedure was given for a calibration using standards of 10, 25, 75, 250, 750, and 2500 ng mL^{-1} for each compound. Figures of merit such as absolute and relative recoveries, precision, and LoD for each biochar and blank concentrations of biochars throughout the whole optimization procedure are given in Table 2. Additionally, absolute and relative recoveries of biochars 2−4 and a 1000 μg kg^{-1} of 16 EPA PAH fortified blank are shown in Figure 4A−D, respectively.

Absolute recoveries of individual PAHs were on average 52 ± 14%, 72 ± 15%, and 42 ± 17% for biochars 2, 3, and 4, respectively (Table 2, Figure 4). They were not statistically different from those obtained for blank controls (58 ± 11%, Figure 4), indicating that losses were not caused by sequestration to biochar, but rather occurring during extraction and solvent removal, probably as a result of evaporation, as indicated by lower percentages of the light PAHs. Not all biochars were equal though, and biochar 4 in particular exhibited rather low absolute recoveries for the heavy PAHs (BbF−BPE, Figure 4). Still, the use of deuterated internal standards allowed us to compensate largely for any such losses, as indicated by relative recoveries of 71 ± 11%, 89 ± 12%, 105 ± 24%, and 98 ± 14% for biochar 2, 3, 4, and the blank control, respectively (Figure 4). These percentages were mostly in the range 70−120%, as requested by good laboratory practice.[18]

The average precision for the Σ16 EPA PAHs was 12 ± 17%, 7 ± 37%, and 4 ± 8% for biochar 2, 3, and 4, respectively (Table 2). Such numbers are overall satisfactory (see, e.g., Kromidas[19]). The lowest precisions were observed for ANA and FLU (e.g., 67% and 141%, respectively, in biochar 3, and 61% and 48%, respectively, in biochar 2), probably as a consequence of their relatively low concentrations and their still considerable volatility.

The LoDs of biochars 2−4 (Table 2) were well below their respective indicated concentrations in Table 1. The concentrations of biochars 2−4 were also above the LoQs, which was 3.3 times the LoD. But some heavy PAHs, such as IPY or BPE in biochar 4, which had the lowest Σ16 EPA PAHs, exhibited concentrations near the LoD. However, LoDs were sometimes surpassed by blank concentrations, particularly in the case of lighter PAHs (Table 2). For NAP, it would rise to 1275 (±837) μg kg$_{dw}^{-1}$ (3 times its blank concentration). This definitely indicates a contamination problem for NAP. Previously, our laboratory encountered considerably lower blank concentrations for NAP ranging from 0.7 to 5.0 μg kg$_{dw}^{-1}$.[10,17,20] The situation is somewhat more pronounced in the case of biochar. One explanation may be the much higher NAP concentrations in biochars than in background soils, sediments, or compost. Another cause that we strongly suspect is some cross contamination of this volatile PAH during the temporally extended toluene solvent removal of several extracts in parallel with a Syncore Analyst apparatus. Usually the situation of elevated NAP blanks was not encountered in between individual sample series, as indicated by roughly 25-times lower blanks in series analyzed quarterly within the International Sediment Exchange for Tests on Organic Contaminants (SETOC) of the Wageningen Evaluating Programmes for Analytical Laboratories (WEPAL).[21,22] Possible measures to minimize this risk for cross-contamination in practice would encompass a switch from parallel to sequential sample processing by rotary evaporation, and reanalyses of low-PAH containing biochars in a separate series. However, both solutions would lead to drastically extended analysis times.

Method Application. This method was developed to quantitatively extract PAHs from biochars. As an example, the concentrations of the 16 EPA PAHs as quantified with the optimized extraction conditions are listed in Table 1. Biochar 3 had the highest ∑16 EPA PAH concentration (355 mg kg_{dw}^{-1}), and biochar 4 had the lowest (9.3 mg kg_{dw}^{-1}). The concentration in biochar 3 was in the same order of magnitude as those measured in traffic, wood, or diesel soot (∑11 PAH: 124, 113, and 233 mg kg^{-1}, respectively).[13] Biochar 2 (63 mg kg^{-1}) exhibited concentrations more comparable to charcoal or oil soot (43 and 59 mg kg^{-1}, respectively).[13] With less than 10 mg kg_{dw}^{-1}, the concentrations of biochars 1 and 4 were like those obtained with a generic analytical method in biochars produced by hydrothermal carbonization or Pyreg.[5]

The majority of the ∑16 EPA PAH consisted of NAP (40−60%), followed by PHE (10−30%). This PAH fingerprint is similar to, e.g., gasoline, but completely different to feedstock used for biochar, such as green waste.[23,24] Moreover, with a median concentration of the ∑16 EPA PAH of 1803 $\mu g\ kg_{dw}^{-1}$ (n = 31;[24,25]), green waste contains considerably less PAHs. Thus, most of the PAHs in the biochars, especially the dominating NAP and PHE, were probably not originally present in the feedstock material, but rather produced during pyrolysis.

Aspects of Biochar Certification and Legislation. To date, the production of biochar is not yet standardized or certified, and its registration not yet institutionalized. However, under the umbrella of the International Biochar Initiative (IBI), biochar producers in Switzerland and the European Union are currently working on a draft version for biochar specification guidelines. In their revised version from Jan 10, 2012, the range of maximum allowed thresholds for the ∑16 EPA PAHs was set at 6−20 mg kg^{-1}. Additionally, by January 2012, producers can get a European Biochar Certificate issued by the control board q.inspectra (Frick, Switzerland). Premium biochar should contain <4 mg kg^{-1} of the ∑16 EPA PAH and basic biochar <12 mg kg^{-1}.

In Switzerland, biochar may be compared with compost and digestate. For such materials, the ordinance on reduction of risks related to handling of chemicals (ChemRRV)[26] states a guide value of 4 mg kg_{dw}^{-1} for ∑16 EPA PAH. Conversely, the ordinance related to impacts on soils (VBBo)[27] sets the soils guide level at 1 mg kg_{dw}^{-1} for the ∑16 EPA PAH, which limits the amount of biochar that could be applied to soil for whatever purpose. Overall, such values seem difficult to meet if this improved extraction method is followed.

Yet a realistic evaluation of biochar amendment as soil improver must also include the assessment of the bioavailable fraction of the PAHs and other organic contaminants in this material. The extent and kinetics of contaminant release for example into the water phase can be measured by passive samplers.[4,13,28,29] A change in legislation toward a realistic evaluation of contaminant burden including the bioavailability is adequate and necessary.

To establish equal conditions for all stakeholders with regards to biochar quality control, registration, and legislation, efforts must clearly be driven toward a harmonized analytical protocol including unified sample preparation and extraction. Contributing to this, we developed a simple, robust, and sensitive extraction method to quantitatively determine total concentrations of PAHs in biochars. This method may serve researchers, practitioners, and legislators to optimize biochar production with a view to minimize its PAH content, to set standards for its registration and legalization, and to properly assess the environmental benefits and risks of this overall promising material.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Pictures of biochars used for method optimization, Hildebrand solubility theory, and raw data of method optimization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Robin Giger for his laboratory work on elemental analysis and surface area determination.

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