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Polycyclic Aromatic Hydrocarbons (PAHs) and Bis(2-ethylhexyl) Phthalate (BEHP) in the Soil of Teff-*Acacia decurrens*-Charcoal Production System in Northern Ethiopia

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Abstract: The current study is aimed at investigating the level of polycyclic aromatic hydrocarbons (PAHs) and bis(2-ethylhexyl) phthalate (BEHP), which pose a potential risk to human health, in soil samples collected from a teff-*Acacia decurrerns*-charcoal production system (TACP system) in northern Ethiopia. Soil samples were collected from the TACP system and from an adjacent teff monocropping system (TM system) from 0 to 20 cm soil depth. Individual PAHs and total concentrations of PAHs and BEHP generally exhibited no significant variation between the TM and the TACP systems over three rotations. In the land-use systems, the mean concentration of PAHs decreased in the order phenanthrene > fluorene > pyrene > chrysene. Fluorene (22.84–24.69 ng g^{-1} dry soil), pyrene (21.99 ng g^{-1}), and chrysene (21.79 ng g^{-1}) were detected in the TACP system only, suggesting that they were from charcoal production. The maximum concentration of BEHP recorded in the soil samples was 104.00 µg g^{-1}, which could be attributed to the polyethylene (PE) bags used for planting the *Acacia decurrens* seedlings of the TACP system. In soil samples, the sum of all PAHs analyzed ranged from not detected (ND) to 170.69 ng g^{-1}, which is below the limits of prevention established by European regulations for soils (3000 ng g^{-1}) and previous studies. Carcinogenic equivalent (BaP-TEQ) and mutagenic equivalent (BaP-MEQ) concentrations calculated for the individual PAHs in the land-use systems ranged from ND to 0.374 ng g^{-1} and from ND to 0.218 ng g^{-1}, respectively, which is far below many international safety standards. Our results indicate that the charcoal production and the use of the charcoal residues as soil amendment in the TACP system is safe concerning soil contamination by PAHs and BEHP and the risk of cancer and mutation.

Keywords: soil contamination; biochar; carcinogenic and mutagenic equivalents; toxic assessment

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Citation: Beshir, M.; Brüggemann, N.; Yimer, F.; Tadesse, M.; Thiele, B.; Hofmann, D. Polycyclic Aromatic Hydrocarbons (PAHs) and Bis(2-ethylhexyl) Phthalate (BEHP) in the Soil of Teff-*Acacia decurrens*-Charcoal Production System in Northern Ethiopia. *Land* **2023**, *12*, 2117. https://doi.org/10.3390/land12122117

Academic Editor: Alexei Konoplev

Received: 13 October 2023
Revised: 16 November 2023
Accepted: 27 November 2023
Published: 29 November 2023

1. Introduction

The teff-*Acacia decurrens*-charcoal production system (referred to hereafter as TACP system) is a unique and rapidly expanding agroforestry system in the Fagita Lekoma district of the northwestern highlands of Ethiopia. In the TACP system, teff (*Eragrostis tef*) and *A. decurrens* trees are intercropped on the same piece of land, where teff is grown in the first year between freshly planted *A. decurrens* saplings, and charcoal is produced for commercial purposes from the wood of *A decurrens* trees after four to five years. Then, the whole cycle is started again on the cleared land, leaving the charcoal residues in the soil below the charcoal production spots. The application of charcoal residues (biochar) to the soil of the TACP system is a strategy to combat land degradation in the district. The application of biochar, a carbon-rich material produced by pyrolysis under low- or no-oxygen conditions during charcoal production, has been used in agriculture to sequester carbon [1,2], reduce greenhouse gas emissions [3,4], improve soil fertility [5,6], enhance crop growth and yield [7,8], and enhance soil adsorption of contaminants [9,10]. However, residual pollutants including polycyclic aromatic hydrocarbons (PAHs) could be generated during biochar production [11–14].

Polycyclic aromatic hydrocarbons (PAHs) are a group of dangerous organic substances containing two or more fused benzene rings, which are found everywhere in the environment [15]. They are byproducts of pyrolytic or incomplete combustion reactions produced when materials containing carbon and hydrogen are heated at temperatures higher than 100–150 °C [16]. These compounds are of particular concern as they are suspected or known carcinogens and mutagens [17,18]. PAHs may enter the environment during the production of charcoal by pyrolysis [19]. They could strongly be adsorbed on soil particles due to their hydrophobicity and low water solubility [20]. Arable top soils typically contain around 200 ng g^{-1} for the sum of the 16 PAHs listed by the U.S. Environmental Protection Agency (US EPA) [21]. Soils contaminated with PAHs can pose a health risk to humans and livestock, as well as an ecotoxicological risk to the soil biome, soil functions, and plants [22]. There are three different PAH exposure pathways for humans: inhalation, ingestion of contaminated food and/or water, and skin contact [23,24]. Therefore, workers involved in the production, transport, and application of biochar may be exposed to a risk when they are in contact with biochar itself or with biochar-amended soils [25,26]. These facts, therefore, justify the need for PAH monitoring in environmental compartments, such as soils [27–29], especially in surface soil due to its role as a large PAH sink in the terrestrial system (>90%) [30].

Several approaches have been developed to obtain a more accurate assessment of potential risk of exposure to a complex mixture of PAHs. In most risk assessments, the benzo(a)pyrene (BaP) toxic equivalent factor is applied to convert other PAH concentrations to BaP-equivalent concentrations for assessing the toxic risks of PAHs, like the BaP toxic equivalent factor (TEF) of [18] and the mutagenic equivalent factor (MEF) of [17], which are used to evaluate the PAHs' carcinogenicity and mutagenicity, respectively. Policymakers and legislators of various countries are working on appropriate thresholds to limit the presence of pollutants in biochar in relation to their use. In this regard, previous studies focused on the analysis of PAHs solely in biochar [13,26]. PAH contents determined in biochar can range widely from 0.1 to even 10,000 mg/kg [12,31]. The maximum limits for the sum of 16 USEPA-PAHs have been defined as 12 mg kg^{-1} of dry mass for the basic grade, according to the European Biochar Certificate [32], and as 6 mg kg^{-1} dry mass according to the International Biochar Initiative certificate guidelines [33]. Both certification initiatives pay particular attention to the formation and accumulation of polycyclic aromatic hydrocarbons (PAHs) during pyrolysis [32].

Despite these defined limits of PAH content in certified biochar, very few studies have evaluated the PAH content of biochar-amended soils [26,34–36]. Furthermore, to our knowledge, no studies so far have addressed the effect of the TACP system on the concentration or level of PAHs and its potential risk to human health. There is also very little information on the effect of soil-applied charcoal residues on the adsorption of bis(2-ethylhexyl) phthalate (BEHP), which is suspected to be present abundantly in the soil of the study area due to the wide use of *A. decurrens* seedling plastic bags for the TACP system. The presence of plastic soil is a serious problem. BEHP is a phthalate ester that is widely used as an additive (as softener or plasticizer) to plastics (e.g., polyvinyl chloride). It has been listed as a priority pollutant by many countries around the world mainly because it disrupts endocrine function in humans and can lead to hepatocellular carcinoma, anovulation, and fetal growth retardation [37]. In order to avoid the risk of BEHP accumulation in humans, it is important to reduce BEHP pollution in soils and crops to minimize the contamination through the food chain and hence to determine the level of BEHP in soil of the TACP system. This report complements previous studies [38,39], in which the same soil samples were analyzed (from 0 to 20 cm depth). The report investigates (1) the effect of the application of the charcoal production residues on the concentration of PAHs in the soil of the TACP system (first, second, and third rotations) as compared with the adjacent TM system; (2) the environmental safety concerning soil contamination and potential human health risk in the study area; and (3) the effect of the application of the charcoal residues on the concentration of BEHP in the soil.

2. Materials and Methods

2.1. The Study Area

The study site is located in the Fagita Lekoma district, Awi zone, Amhara Region of northwestern Ethiopia (10°57′23″ N to 11°11′21″ N, 36°40′01″ E to 37°05′21″ E; 1800–2900 m above mean sea level) (Figure 1). The long-term (2000 to 2017) mean annual rainfall of the area is 1328 mm [40] with an average annual temperature of 17.5 °C [41] (Figure 2). The area is part of the moist subtropical agroecological zone of the northwestern highlands of Ethiopia. The predominant soil types are Nitisol and Acrisol, and they are of moderately acidic pH [42,43]. Major physicochemical properties of soils of the study area are presented in Table 1. The area is characterized by flat lands and moderately steep rolling topography [40]. The major land-use categories of the district are agriculture (60.8%) and forest (19.5%), while the remaining area is grazing land and settlement [44].

Table 1. Physicochemical properties of soil samples from the TM and TACP systems for depth 0–20 cm: textural fractions (%), pH, soil organic carbon (SOC) (%), bulk density (Bd) (g cm^{-3}), and total nitrogen (TN) (%).

Soil Properties	**Land-Use Types**			
		TACP System		
	TM System	**Rotation 1**	**Rotation 2**	**Rotation 3**
Sand	29.67	29.21	29.25	26.75
Silt	29.42	29.20	29.25	30.30
Clay	40.92	41.78	41.20	42.87
pH	5.06	4.48	4.65	5.02
SOC	2.34	4.19	4.10	1.87
Bd	0.76	0.90	0.87	0.81
TN	0.20	0.35	0.32	0.19

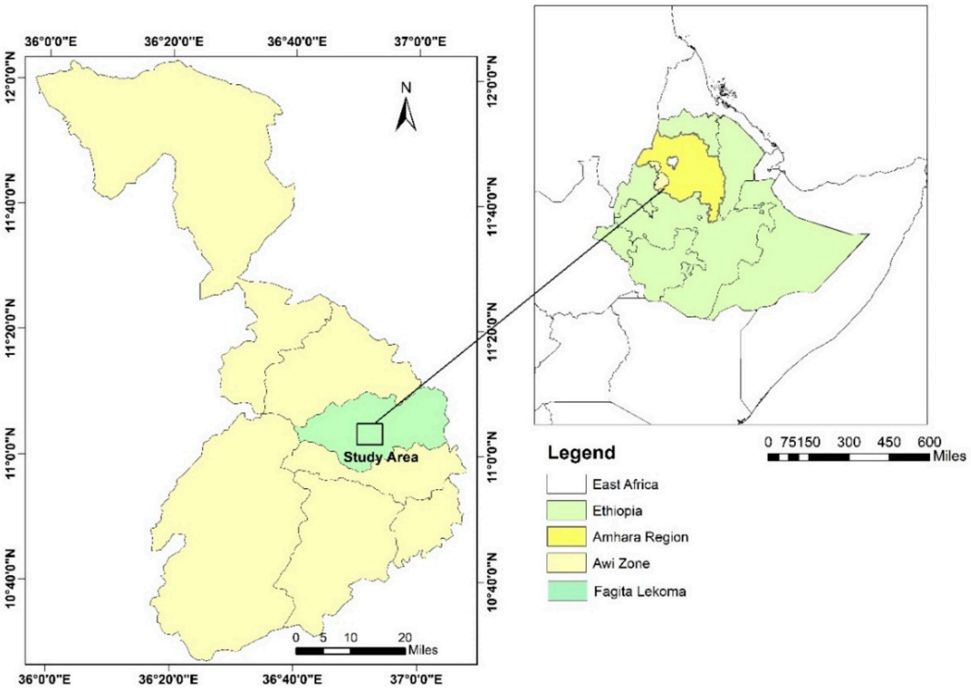


Figure 1. Map of the study area.

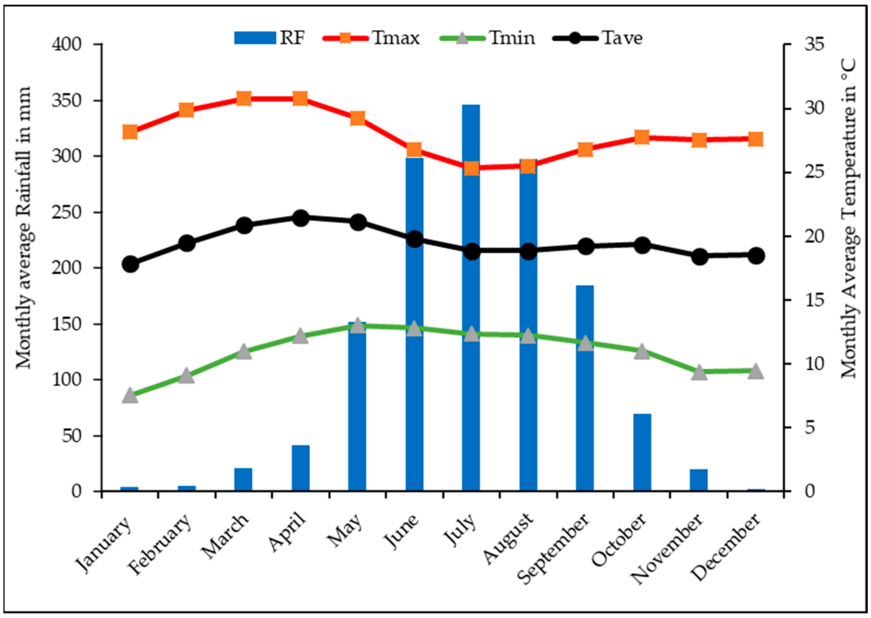
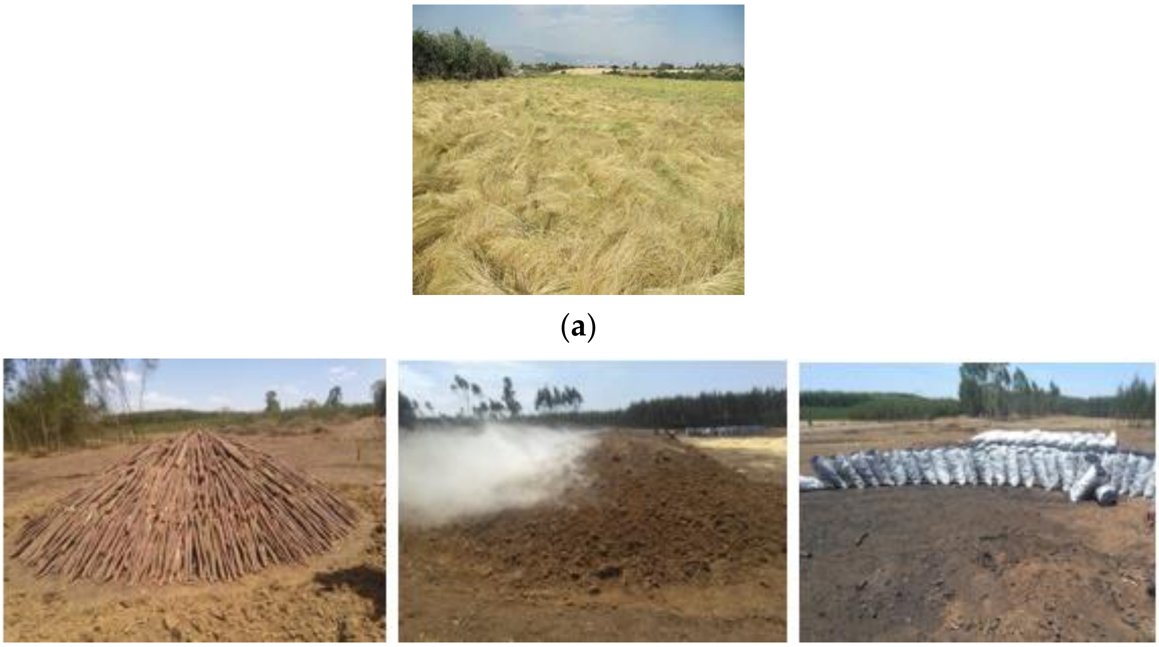


Figure 2. Maximum, minimum, and average temperatures and mean monthly rainfall of Fagita Lekoma district, from 2007 to 2017 (The data used in this figure were extracted with permission from [45].

2.2. The TM and TACP Systems

Parts of the TM and the TACP system are depicted in Figure 3. TM system is conventional teff cropping system wildly practiced in the study area (Figure 3a). In TM system, teff fields are tilled by oxen at least four times up to 20 cm depth from April to end of May to smooth the land. Teff is a staple crop in Ethiopia, where it is used mainly to make injera—a spongy flatbread that is eaten with most meals. The main fertilizers used in the TM system are urea and diammonium phosphate (DAP) and potassium fertilizers by some farmers. The urea and the DAP are applied mostly at the same rate of about 50 kg ha^{-1}, and the application rate of both varies between 40 and 60 kg ha^{-1} depending on the socioeconomic status of the farmer [46,47]. In addition to the urea and the DAP, about 10 Mg/ha of cattle manure is also spread before the fourth tilling, which starts 7 days after the third. During the fourth tilling, any weeds are removed from the field and the seedbed is prepared. Teff is harvested manually in October and threshed in December. The teff residues are used as animal feed or for local mud house construction. Livestock is allowed to enter the TM system for grazing after teff is harvested.

TACP system (Figure 3b) is rotational practice of teff *A. decurrens* intercropping and charcoal production. In TACP system, *A. decurrens* seedlings are planted in the teff fields at about 25–50 cm spacing. The teff is grown in the first year and harvested after 3 to 5 months, whereas *A. decurrens* is grown for about 4 to 5 years. After the harvesting of teff at the end of the second year, local farmers let grasses grow beside *A. decurrens*. They use the grass for sale or to feed their own livestock. In the third and fourth years, the trees continuously grow without teff and grass cultivation. And after about four to five years, charcoal is produced on the same pieces of land for commercial purposes from wood of *A. decurrens* trees like in the traditional mound kilns in Figure 3b. Then, the whole cycle is started again on the cleared land, spreading the charcoal residues in the soil of the TACP system (in and outside of charcoal production spot) for its potential of improving soil fertility. In the TACP system, *A. decurrens* seedings are prepared using polyethylene bags, which were hypothesized in this study to cause bis(2-ethylhexyl) phthalate (BEHP) contamination in the TACP and its vicinity including the TM system.



(**a**)

(**b**)

Figure 3. TM system (**a**) and a charcoal production in the TACP system (**b**) (Photos© Miftha Beshir, 2018).

2.3. Soil Sampling

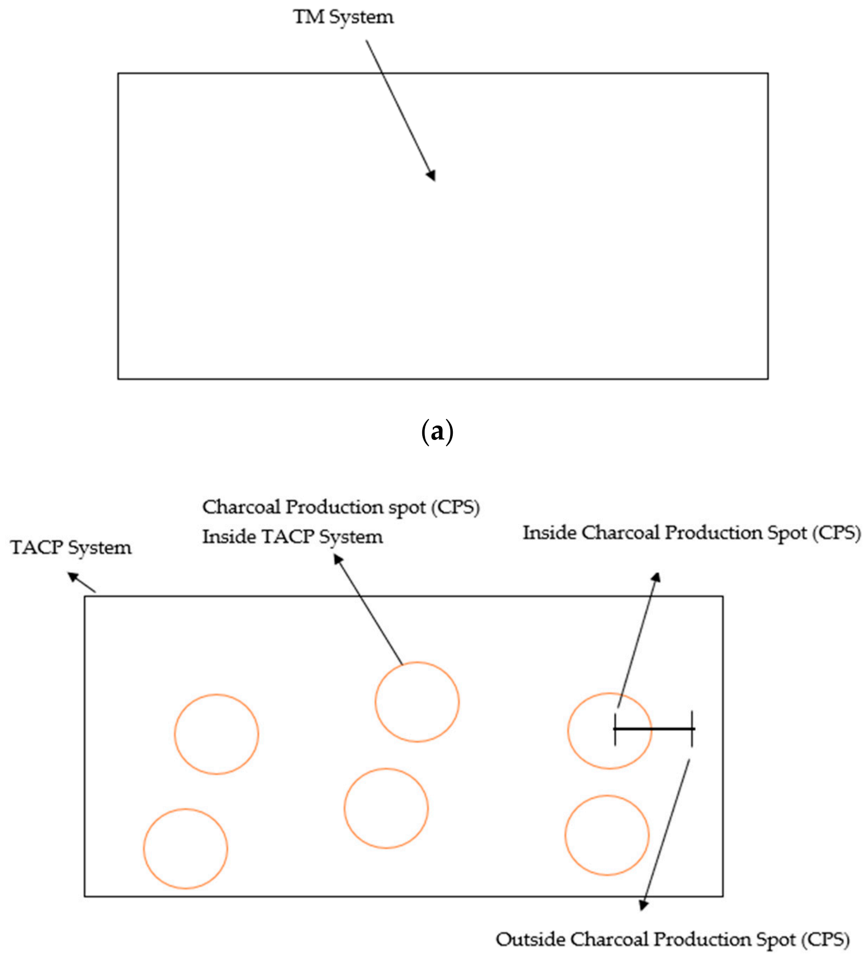
The soil samples were collected from the TM and the TACP systems (Figure 4a,b) with four replicates from 0 to 20 cm depth after teff harvest. In the TACP system, soil samples were collected from inside and outside of six randomly selected charcoal production spots (Figure 4a) and then mixed and homogenized to a single composite soil sample for each field replication. Together, the sampling design covered three different areas (in TM system and inside and outside of the charcoal production system of TACP system in the first and second and third rotations) as treatments (Figure 4a,b), resulting in a total number of 28 composite soil samples (7 treatments × 4 replications × 1 depth). Soil samples were taken only from same horizontal planes of fields, plots, and rotations and with similar number of charcoal production spots to keep the similarity among treatments.

2.4. Analysis of Soil Properties

Soil samples for chemical analysis were passed through a 2 mm soil sieve. Soil texture was determined using the hydrometric method after removing SOM using hydrogen peroxide and thereafter dispersing the soil with sodium hexametaphosphate [48]. The USDA particle size classes for sand (2.0–0.05 mm), silt (0.05–0.002 mm), and clay (<0.002 mm) were used for assigning the textural classes. Bulk density was determined by using the core method [48]. Soil pH was measured with electrodes in a 1:2.5 soil/water suspension. Soil organic carbon (SOC) was determined by using the Walkley–Black oxidation method [49]. Total nitrogen (TN) was measured with the Kjeldahl digestion method [50].

2.5. Analysis of Polycyclic Aromatic Hydrocarbons and Phthalates

Chemicals: PAH standard mix (certified reference material EPA 525 PAH Mix B (13 PAHs), 500 mg/L of each component in acetone, VWR, Darmstadt, Germany), dibutylphthalate, diisooctylphthalate, diisodecylphthalate, and bis(2-ethylhexyl)phthalate (BEHP) were purchased from VWR (Darmstadt, Germany). Methanol and acetone (both LC-MS grade) were also supplied by VWR (Darmstadt, Germany).



(**a**)

(**b**)

Figure 4. Soil samples were taken from TM system (**a**) and inside and outside of the charcoal production spot of the TACP system (**b**).

Accelerated solvent extraction (ASE): PAH/phthalate extraction was carried out using an ASE instrument 350 (Thermo Fisher, Waltham, MA, USA). Approximately 7 g dry soil sample was mixed with the same volume of diatomaceous earth (Merck, Darmstadt, Germany) and filled in a 22 mL stainless steel cell. The bottom and top of the cell were covered by glass fiber filters (Thermo Fisher, Waltham, MA, USA). The ASE program was set as follows: the extraction solvent was methylene chloride/acetone (1:1 *v*/*v*); extraction temperature was set at 100 °C; static extraction time was 5 min; and the number of static cycles was 1. The purge volume was set at 60% and the purge time at 60 s. The obtained extracts (approximately 40 mL) were evaporated to dryness in a stream of nitrogen. The residues were reconstituted in 1 mL acetone. While samples were directly analyzed for PAHs, samples for the determination of phthalates were diluted by a factor of 15. For determination of the phthalate blank value of the plastic bottles used for soil sampling, 1 g plastic was cut into small pieces and extracted by the same ASE procedure.

Quantification of PAHs and phthalates by gas chromatography–mass spectrometry (GC–MS) analysis: The GC–MS system consisted of an Agilent 7890B gas chromatograph and equipped with 7693 autosampler (Santa Clara, CA, USA) as well as a Jeol JMS-T200GC AccuTOF GCx mass spectrometer (Tokyo, Japan). PAHs were separated on an Optima 1701 MS column (30 m × 0.25 mm i.d., 0.25 µm film thickness) (Macherey-Nagel, Düren, Germany) and phthalates on a ZB-5 HT Inferno column (30 m × 0.25 mm i.d., 0.25 µm film thickness) (Phenomenex, Torrance, CA, USA). Helium was used as carrier gas at a constant gas flow of 1.0 mL/min. The oven temperature program employed for the analysis of

PAHs was as follows: 100 °C, with 8 °C/min to 300 °C, which was held for 15 min (total runtime: 40 min). Phthalates were analyzed by use of the following temperature program: 50 °C, with 4 °C/min to 340 °C, which was held for 1 min (total runtime: 73.5 min). The injector temperature was held at 250 °C (PAHs) and 290 °C (phthalates), respectively, and all injections (1 µL) were made in split mode (1:10). The mass spectrometer was used in the electron ionization (EI, 70 eV) mode and scanned over the range m/z 40–750 with a sampling interval of 0.25 ns and a recording interval of 0.4 s. The GC interface and ion chamber were kept at 290 °C and 250 °C, respectively. Data processing was performed by use of the software MSAxel (Jeol) version 5.3 and XCalibur 2.0.7 (ThermoFisher Scientific, Waltham, MA, USA). Quantification was performed by the method of external calibration with standard solutions in the concentration range 0.05–2.0 mg/L for PAHs and 5.0–50 mg/L for phthalates.

2.6. Calculation of BaP-Equivalent Concentrations

BaP-TEQ (carcinogenic equivalents, ng g^{-1}) and BaP-MEQ (mutagenic equivalents, ng g^{-1}) were calculated by multiplying the concentrations of each PAH compound with its toxic equivalency factors (TEFs) for cancer potency relative to BaP [18] and mutagenic potency factor (MEF) relative to BaP [17], respectively. BaP-TEQ and BaP-MEQ for each land-use type were described by Equations (1) and (2), respectively.

$$\text{(BaP-TEQ) PAH} = \sum C_n \, \text{TEF}_n \tag{1}$$

$$\text{(BaP-MEQ) PAH} = \sum C_n \, \text{MEF}_n \tag{2}$$

where C_n = concentration of individual PAH compound (n) and TEF_n = toxic equivalent factor for individual PAH compound (n). MEF_n = mutagenic equivalent factor for individual PAH compound. In the present study, the TEFF_n of the seven carcinogenic PAHs: BaA, Chr, BbF, BkF, BaP, IcdP, and DahA were 0.1, 0.01, 0.1, 0.1, 1, 0.1, and 1 and the MEF_n of value for BaA, Chr, BbF, BkF, BaP, IcdP, and DBhA were 0.082, 0.017, 0.25, 0.11, 1, 0.31, and 0.29, respectively [17].

2.7. Statatistical Analysis

The data were then grouped according to the land-use types (the TM and the TACP systems in three rounds). Statistical differences were tested using an analysis of variance (ANOVA) following the general linear model (GLM) procedure of SPSS Version 20.0 for Windows [50]. Tukey’s honest significance difference (HSD) test was used for mean separation when the analysis of variance showed statistically significant differences ($p < 0.05$).

3. Results

3.1. Level of PAHs

The individual and total concentrations of PAHs found in the TM system and the TACP system are shown in Table 2. Only compounds with a value above detection (quantification limit) were considered for calculating the sums. No statistical difference in the concentration of phenanthrene was detected between the TM and the TACP systems and among the three rotations (Table 2). The maximum concentration of phenanthrene detected in all soil samples was 136.41 ng g^{-1}.

Among the 13 PAHs in the 28 samples analyzed, only 4 PAHs were detectable (Table 2). Fluorene, pyrene, and chrysene were detected in the TACP system only. Phenanthrene was observed in 100% of the soil samples. The detection rate of chrysene (10.71%) was relatively low. Fluorene was detected in 28.57% of the samples, while pyrene was detected in 17.86% of the samples. Acenaphthylene, anthracene, benzo(a)anthracene, benzo(k)fluoranthene, benzo(b) fluoranthene, benzo(a)pyrene, indeno(1,2,3c,d)pyren, benzo(g hi) perylene, and dibenzo(ah) anthracene were not detected in any of the samples studied (Table 2). In the land-use systems, the mean concentration of PAHs decreased in the order penanthrene > fluorene > pyrene > chrysene (Table 2).

Table 2. Mean concentration of PAHs in the land-use types, TM and TACP systems (ng g^{-1}) (fluorene (Flu), acenaphthylene (Ace), phenanthrene (Phe), anthracene (Ant), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(k)fluoranthene (BkF), benzo(b)fluoranthene (BbF), benzo(a)pyrene (BaP), indeno(1,2,3-c,d)pyren (IcdP), benzo(ghi)perylene (BghiP), and dibenzo(ah)anthracene (DBahA)).

PAHs [ng g^{-1}]	Land-Use Types			
		TACP System		
	TM System	Rotation 1	Rotation 2	Rotation 3
Flu	ND	22.84	24.69	ND
Ace	ND	ND	ND	ND
Phe	42.42	66.34	61.42	58.10
Ant	ND	ND	ND	ND
Pyr	ND	ND	ND	21.99
BaA	ND	ND	ND	ND
Chr	ND	ND	ND	21.79
BkF	ND	ND	ND	ND
BbF	ND	ND	ND	ND
BaP	ND	ND	ND	ND
IcdP	ND	ND	ND	ND
BghiP	ND	ND	ND	ND
DBahA	ND	ND	ND	ND
Total	42.42	89.18	86.11	101.88

In the present study, there was no significant variation in the total concentration of PAHs (∑PAH) between the TM and TACP systems and among the three rounds (Table 2). Fluorene, pyrene, and chrysene were not detected in all the samples and treatments. Fluorene (24.69 ng g^{-1}), pyrene (21.99 ng g^{-1}), and chrysene (21.79 ng g^{-1}) were detected in the TACP system only (Table 2). The ∑PAH were 42.42, 89.18, 86.11, and 101.88 ng g^{-1} for the soil of the TM system and rotations 1, 2, and 3 of the TACP system, respectively (Table 2). The overall mean ∑PAH for the two land uses was 79.89 ng g^{-1}. And the (∑PAH) varied between 37.98 ng g^{-1} and 49.54 ng g^{-1} in the TM system and between 12.68 ng g^{-1} and 170.69 ng g^{-1} in the TACP system. No statistical difference in the concentration of phenanthrene was detected between the TM and the TACP systems and among the three rotations (Table 2). The maximum concentration of phenanthrene detected in all soil samples was 136.41 ng g^{-1}.

3.2. *Toxic Assessment*

The BaP-equivalent (BaP-TEQ and BaP-MEQ) concentrations were calculated for the individual carcinogenic PAH measured. The BaP-TEQ for all soil samples ranged from 0 to 0.374 ng g^{-1} dry soil, while the BaP-MEQ ranged from 0 to 0.218 ng g^{-1} for all soil samples. In our study, of all the PAHs, exclusively chrysene contributed to BaP-TEQ and BaP-MEQ in a few soil samples of rotation 3 of the TACP system.

3.3. *Bis(2-ethylhexyl) Phthalate (BEHP)*

No statistical difference in the concentration of BEHP was delectated between the TM and the TACP systems and among the three rounds (Figure 5). The maximum concentration of BEHP detected in the soil samples was 104.00 μg g^{-1}.

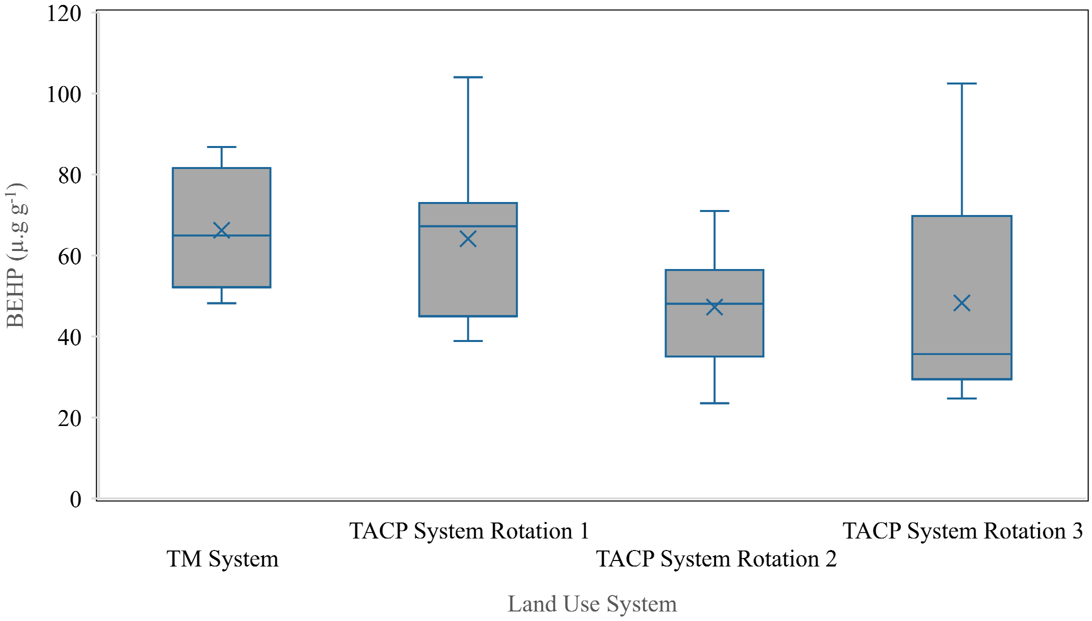


Figure 5. Mean BEHP concentrations in the soil of the TM system and the different rounds of the TACP system. Means marked with the same letters do not differ statistically by using Tukey's test (p = 0.05). Vertical bars denote the standard deviation.

4. Discussions

4.1. Level of PAHs

In this study, the concentration of PAHs showed no significant variation between the TM and the TACP systems in the three rotations.

The relatively large, though not statistically significant, increase in phenanthrene in the TACP round system as compared with the TM system (Figure 3) was probably related to the charcoal production from which charcoal residues were added to the soil as biochar. Phenanthrene was reported to be the second most abundant PAH in biochar [11,12,26,31] after naphthalene [51].

In the present study, the absence of fluorene, pyrene, and chrysene in all samples and treatments suggests that they were introduced with the charcoal debris into the soil. Previous studies revealed that PAHs are strongly sorbed by biochar and biochar-amended soil [52–54]. Hale et al. [11] reported that biochar derived from different types of wood could adsorb 70–3270 ng g^{-1} of PAHs. The dominant PAHs pyrene and chrysene in the TACP system could be due to the fact that higher-molecular-weight PAHs are more strongly adsorbed to carbonaceous sorbents than lower-molecular-weight PAHs [55], corresponding to the relatively higher content of soil organic carbon (4.19%) in the TACP system [39].

The obtained values of total concentrations of PAHs in two land-use systems (42.42 to 86.11 ng g^{-1}) in this study were lower than those commonly reported in the literature [26,36,51,56]. The relatively, but not significantly, higher total concentration of ∑PAH in the TACP system in the present study was probably due to charcoal debris left in the soil of the TACP system. Previous studies (e.g., [35,57,58]) revealed that PAHs are strongly sorbed by biochar and biochar-amended soil.

In this study, none of the PAH concentrations approached the maximum permitted levels established, indicating that soils in the TACP system contained PAHs below the limits of prevention established by European regulations for soils (3000 ng g^{-1}) and also lower than the findings of previous studies about biochar-amended soils [26,36,51,56].

In another classification system suggested by [59], ∑PAH values in agricultural soils <200 ng g^{-1}, 200–600 ng g^{-1}, 600–1000 ng g^{-1}, and >1000 ng g^{-1} were defined as "non-contaminated", "weakly contaminated", "contaminated", and "heavily contaminated", respectively. According to this classification, both the TM and the TACP systems could be classified as “non-contaminated”. The relatively low PAH concentrations could be attributed to the dominance of the three-ring compounds phenanthrene and fluorine, and the four-ring compounds pyrene and chrysene, which are low-molecular-weight compounds [60]. In addition, these compounds are among the PAHs most susceptible to leaching and degradation within the groups of PAHs, and they are also among the most volatile compounds, which makes them less abundant [60,61].

4.2. Toxic Assessment

In the present study, the BaP-TEQ and BaP-MEQ concentrations were far below the values reported in different countries for soils modified through human activities. For instance, 9.0 ng g^{-1} and 10.6 ng g^{-1} in Norway [62]; 26.9 ng g^{-1} and 22.1 ng g^{-1} in Korea [63]; 217.6 ng g^{-1} and 150.8 ng g^{-1} in India [64]; 17.9 ng g^{-1} and 20.0 ng g^{-1} in Italy [65]; 20.1 ng g^{-1} in China [66]; and 64.1 ng g^{-1} in Spain [66] for a soils treated with biochar. By comparison, the BaP-TEQ and BaP-MEQ concentrations in this study were at a relatively low level in a global context. The BaP-TEQ concentration of this study is far less than the safe level of 260 ng g^{-1} in soil [67] based on the Netherlands National Institute of Public Health. And the BaP-MEQ concentration is also far less than the safe level of 600 ng g^{-1} based on the risk-based soil criterion for the protection of human health of the Canadian Council of Ministers of Environment [68]. The BaP-TEQ and BaP-MEQ were also less than the screening or threshold value (550 ng g^{-1}) so that the contamination risk posed by pollutants to the soil environment can be ignored according to the soil environmental quality risk control standard for soil contamination of agricultural land [69].

4.3. Bis(2-ethylhexyl) Phthalate (BEHP)

In the present study, the concentration of BEHP exhibited no significant variation between the TM and the TACP systems in the three rotations.

The lower but not statistically significant concentration of BEHP in the TACP system than in the TM system was very likely because the charcoal debris in the TACP system strongly adsorbed BEHP. The relatively higher SOC in the first and second rounds of the TACP system could also play a role (Table 1) because easily available organic carbon provides energy for microbes and promotes microbial activity, which has been found to be positively and significantly correlated with the degradation rates of BEHP [70]. Similar types of degradation have been reported in other studies (e.g., [71,72]). The relatively but not significantly higher mean concentration of BEHP (Table 2) in the TM system could be attributed to the polyethylene (PE) bags used for planting the *A. decurrens* seedlings of the TACP system in the study area. BEHP is a widely used plasticizer for many kinds of polymers, such as PE and PVC [72], and it is a serious environmental problem in areas where agricultural plastic films are used intensively [73,74].

5. Conclusions

The charcoal production in the TACP system did not affect the concentration of PAHs and BEHP. The concentrations exhibited no significant variation between the TM and the TACP systems in the three rotations.The concentration of PAHs in the two land-use systems is generally below the maximum level established by international guidelines and previous studies. The PAHs in the two land-use systems originated mainly from the charcoal production in the TACP system, whereas the BEHP originated from the polyethylene (PE) bags of the Acacia decurrens seedlings. In the two land-use systems, the BaP-TEQ ranged from ND to 0.374 ng g^{-1} and the BaP-MEQ from ND to 0.218 ng g^{-1}. They are less than the screening or threshold value (550 ng g^{-1}), according to the soil environmental quality risk control standard for soil contamination of agricultural land, meaning that the contamination risk posed by pollutants to the soil environment can be ignored. Therefore, the charcoal production and the use of the charcoal residues for soil amendment in the TACP system is safe concerning soil contamination by PAHs and BEHP and risk of cancer and mutation. However, the production of chrysene (which contributed 100% of the BaP-equivalent concentration) and BEHP due to the plastic seedling bags in the TACP should draw specific attention in future studies. Moreover, without a doubt, the effect of the TACP system on PAH and BEHP concetrations in the study area requires further research. Also, without any doubt, the charcoal debries in the TACP system should be thouroughly studied prior to application for soil amendment.

Author Contributions: Conceptualization, M.B., N.B. and F.Y.; methodology, M.B., N.B. and F.Y.; software, M.B.; formal analysis, M.B.; investigation, M.B.; resources, N.B.; data curation, M.B.; writing—original draft preparation, M.B.; writing—review and editing, M.B., N.B., F.Y., M.T., D.H. and B.T.; supervision, N.B., F.Y. and M.T.; polycyclic aromatic hydrocarbons and bis(2-ethylhexyl) phthalate analysis, D.H., B.T. and M.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Forschungszentrum Jülich, Germany.

Data Availability Statement: The datasets analyzed in this study are available from the corresponding author on reasonable request.

Acknowledgments: M.B. is grateful to all the field workers and lab technicians for their field and lab assistance.

Conflicts of Interest: The authors declare no conflict of interest.

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