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Procedure to Measure the Level of Polycyclic Aromatic Hydrocarbons in Wood Ashes Used as Fertilizer in Agroforestry Soils and Their Transfer from Ashes to Water

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Before wood ash can be safely used as a fertilizer in soils, possible negative effects such as input of organic contaminants or remobilization of contaminants already stored in the soil must be investigated. The objective of this study was to optimize and characterize extraction methods to isolate and quantitatively measure polycyclic aromatic hydrocarbons (PAHs) concentrations in wood ash that can be used as amendment of soils. It will be then possible to examine the effects of wood ash application on PAHs concentrations in the washing waters with the aim of evaluating their distribution by storage in the different compartments and what influences their stability and persistence. Simple, rapid and inexpensive methods have been set up for the determination of seven polycyclic aromatic hydrocarbons (PAHs) in wood ashes and ash aqueous extracts without interferences from other chemical contaminants using organic solvent extraction and/or SPE techniques and analyzed by an optimized RP-HPLC-FLD method. The feasibility of extraction for the determination of PAHs in wood ashes has been evaluated because PAHs are strongly sorbed to such a matrix, which explains why the PAHs content in ash was seldom studied. The method resulted to be of recoveries ranging from 81 to 97% for the different PAHs, with repeatabilities (RSDs%) better than 6%. Detection levels were from 0.2 to 2.2 μg/kg, while quantification limits were from 0.7 to 5.6 μg/kg, low enough to evaluate the presence of PAHs in wood ashes.

KEYWORDS: PAHs; wood ash; waters; HPLC-FLD

INTRODUCTION

In many countries, wood ash is used as a fertilizer in forests (*1*). However, wood ash can only be safely used in forests if negative effects are small in comparison with benefits (*2*). Wood ash is known to contain significant concentrations of heavy metals and other contaminants, but little is known about the concentrations of polycyclic aromatic hydrocarbons (PAHs) and their fate after addition to the soil. Furthermore, PAHs are already present in most soils, because they are ubiquitously distributed and are persistent in different ecosystems (*3*, *4*). Due to high rates of interception deposition, forest soils receive particularly high inputs of organic contaminants from the atmosphere that mainly accumulate in the organic layer (*5*−*7*). After applying wood ash onto a forest soil, the increase in pH might lead to increased dissolved organic matter (DOM) and to an enhanced mineralization. This might result in a mobilization of already accumulated organic contaminants and in a redistribution of PAHs due to DOM-facilitated transport (*8*, *9*).

The published data on concentrations of organics in wood combustion ashes is quite limited. Although PAHs are formed during the combustion process and high concentrations were measured in fumes and particles emitted from wood fires (*10*, *11*), the ash itself was seldom studied. Other authors used a method for soil samples and applied it to wood ashes without controlling recovery, precision and quantification limits for PAHs in such a matrix (*12*). In any case, they found in the wood ash used in their experiment a ΣPAHs concentration of 16.8 mg kg^{-1}. This was rather high and nearly reached the proposed threshold value of 20 mg kg^{-1} for the application of secondary materials to agricultural field soils (*2*). It was also high compared with the concentrations in the forest soil, and with annual deposition rates. These were estimated to be 2 to 4 mg m^{-2} yr^{-1} for Germany, and approximately 0.8 mg m^{-2} yr^{-1} for the UK (*4*, *13*). Therefore, a PAH input with 8 Mg wood ash ha^{-1} equals approximately 3 to 16 times the annual atmospheric deposition rate.

When ashes are used as soil amendments, PAHs may attach to small particles and be transported by rainfall to streamwaters. Preferential flow of waters and solutes has been shown for a

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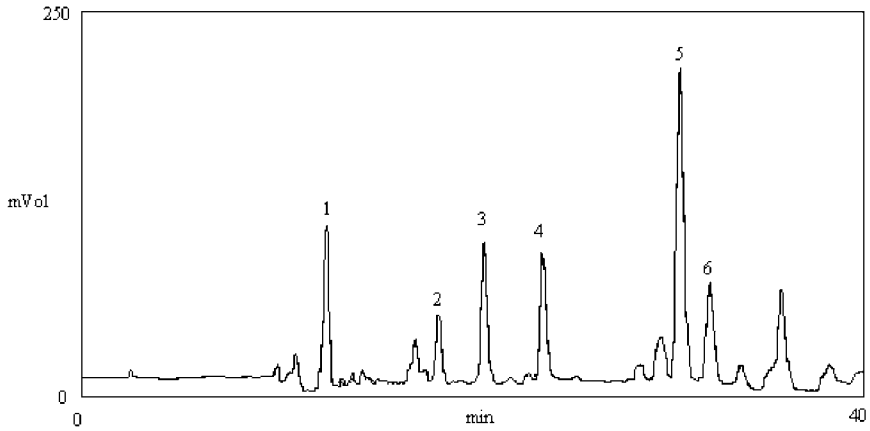

Figure 1. Chromatograms obtained for fired *Populus* matches with the selected wavelength detection program. Peaks identification: B*[a]*A (1), B*[b]*F (2), B*[k]*F (3), B*[a]*P (4), B*[ghi]*P (5), and I*[1,2,3-cd]*P (6).

large variety of soils (*14*−*16*). Colloidal matter, suspended solids, and dissolved organic matter (fulvic and humic acids) in runoff and streamwaters may affect the partition or adsorption processes of PAHs (*17*), because their association with these substances is energetically favorable (*18*, *19*) and can lead to an enhanced overall water solubility (*8*) and altered availability (*20*). In this paper, we contribute to report how two different extraction techniques (organic solvent extraction followed by solid phase extraction or SPE) can be satisfactorily used to quantitatively extract PAHs from wood ash. There are many methods for quantification of PAHs in agricultural and environmental samples (crops, soils, sediments, wastewater, etc.), but there is still a necessity for such a method with wood ashes.

MATERIALS AND METHODS

Chemicals and Materials. The seven PAHs studied (benzo[*b*]fluoranthene (B[*b*]F, 98%), benzo[*k*]fluoranthene (B[*k*]F, 98%), benzo[*a*]pyrene (B[*a*]P, 97%), benzo[*ghi*]perylene (B[*ghi*]P, 98%), indeno[1,2,3-*cd*]pyrene (I[1,2,3-*cd*]P, 98%), benzo[*a*]anthracene (B[*a*]A, 98%), and dibenzo[*ah*]anthracene (DB[*ah*]A, 97%)) were purchased from Aldrich and Supelco. The first five are indicators of drinking water quality (*21*), whereas it is important to monitor the rest in environmental (wild animals, soil, particulate matter in air, etc.) and food (oil, fried foods, etc.) samples. Acetonitrile, water, dichloromethane, acetone, ethyl acetate, and hexane of HPLC grade were supplied by Merck. Cetyltrimethylammonium bromide salt (CTABr, 99%), sodium hydroxide (98%), and hydrochloric acid (37%) were supplied from Panreac.

Waters Sep-Pak silica (690 mg) or octadecylsilica (360 mg) cartridges were used as solid-phase extraction (SPE) minicolumns for purification and concentration. A Visiprep Solid Phase Extraction Vacuum Manifold was used to simultaneously process up to 24 SPE cartridges. The Visidry Drying Attachment was used to dry up to 24 SPE cartridges at one time and can be used with any inert gas supply. Nitrogen C-45 of analytical quality was supplied by Carburos Metálicos. Other small apparatus such as a rotary evaporator, an ultrasonic bath, an up-and-down shaker, an oven, an analytical scale, and a vortex shaker were used. Among other disposables, a sieve (0.2 mm), nylon filters (0.45 μm), micropipets (200−1000 μL) and injection vials (2 mL) provided with screw caps and PTFE-lined butyl rubber septa and inserts (0.35 mL) were used.

Preparation of Standard Solutions. Independent 100 mg/L stock solutions of PAHs were prepared by dissolving about 0.01 g of the different PAHs in a small amount of hexane and diluting to 100 mL with the same solvent. From this solution, a PAHs mix solution at levels ranging from 1 to 2 mg/L for the different PAHs was prepared into acetonitrile by previously evaporating hexane. These solutions were stored in amber flasks at 4 °C and were then stable for at least 6 months. From the PAHs mix solution, different calibration solutions in acetonitrile at levels ranging from 2 to 175 μg/L were prepared to construct twelve-point calibration lines for the PAHs. All these solutions were preserved for at least 2 months in the same storage conditions.

Table 1. Wavelength Detection Program for Quantification of PAHs

PAHs	time window (min)	λexc (nm)	λem (nm)	gain	slit (nm)
B[*a*]A	0–15	288	388	10	40
B[*b*]F & B[*k*]F	15–22	300	446	10	40
B[*a*]P & D[*ah*]A	22–30	296	406	10	40
B[*ghi*]P & I[*1,2,3-cd*]P	30–40	289	432	100	40

Chromatographic Conditions. All HPLC measurements were taken using a Thermo Separation Products (TSP) P2000 binary pump, equipped with a TSP AS1000 autosampler, a TSP SCM1000 vacuum membrane degasser and a Jasco FP-1520 fluorescence detector. The chromatographic data were collected and processed using the ChromCard software. The optimized instrumental parameters for the chromatographic analysis of PAHs (**Figure 1**) were as follows:

Injection Loop. 50 μL.

Column. A 25-cm × 4.6-mm i.d. stainless steel analytical column packed with 5-μm Supelcosil LC-PAH (Supelco).

Elution Conditions. A 32-min linear gradient elution from 80:20 acetonitrile/water to 97:03 acetonitrile/water, followed by a 3 min isocratic elution and 2 min linear gradient to 100% acetonitrile, keeping 100% acetonitrile for 5 min. The utilization of mobile phase components such as acetonitrile and water, which are compatible with atmospheric pressure ionization techniques of mass spectrometric detection, allows the employment of such techniques in the case of the need of a confirmation procedure for the identification of the separated peaks as PAHs. Flow rate was 1 mL/min throughout. Elution temperature was mantained at 33 °C. A column heater programmed at constant temperature was necessary to obtain reproducible PAHs retention times. It is of paramount importance to use a defined wavelength program, which allows the optimization of sensitivity and specificity for each PAH.

Fluorescence Detection. Excitation and emission fluorescence spectra were recorded for the different PAHs, with the intention of selecting the most appropriate detection wavelengths according to the best compromise between fluorescence response and selectivity (**Table 1**). In the case of the analysis of waters in the search for PAHs, the gain all along the wavelength program was kept at 1000. It is possible to perform a second injection with a different detection program to confirm the identity of the PAHs detected by changing wavelengths in all time windows and doing response ratios, which are characteristic for each PAH and independent of concentration.

Samples. Ash samples were obtained according to different procedures from the following species: *Pinus pinaster*, *Eucalyptus globulus*, *Ulex galii*, and *Erica cinerea*. The materials were dried at 100 °C for 24 h and then cut into small pieces before being submitted to the following combustion procedures: Ashes were obtained by heating the material in an oven at 300 °C for 15 min, limiting the oxygen input to

a minimum (no PAHs were found in such ashes obtained by oven combustion; they were fortified with PAHs and used for method characterization). Ashes of those materials were also obtained by ignition and catching fire with a flame, together with ashes from *Populus sp*. matches also obtained by match-like combustion (the content of PAHs in these samples was measured repeating the experiments four times; those from *Populus sp.* matches were used for method optimization).

Water extracts of the *Populus sp.* matches ashes were obtained as follows: 0.3 g ashes were mixed with 300 mL of water, and the mix was magnetically stirred for 15 min, keeping the temperature at that usual in the water around 12 ± 2 °C. The ashes weight/water volume ratio of 1 g/L was selected according to the level of fertirrigation with secondary materials applied to crops; it is also similar to the ratio between the average ash production in a forest fire and the average rainfall in Summer in Galicia (NW Spain).

Sample Treatment. Ashes were sieved (<0.2 mm). In an amber glass vial, 0.1 g of ashes were extracted with dichloromethane (10 mL) in an ultrasonic bath at 40 °C for 10 min. The solvent was separated by filtering through nylon membranes (0.45 μm) and then rotary evaporated to dryness; the residue was subsequentely redissolved in hexane (5 mL). The hexane solution was cleaned-up with a silica cartridge, passing through the cartridge additional hexane (9 mL) to complete PAHs elution. The collected hexane solution was taken to dryness by rotary evaporation, and the residue obtained was redissolved in acetonitrile (1 mL). The new solution was filtered through nylon membranes (0.45 μm) and 50 μL were injected into the chromatographic system.

Ash aqueous extracts were filtered through nylon membranes (0.45 μm) and then extracted by SPE with octadecylsilica (ODS) cartridges according to our own experience (*22*). To sum up, ODS cartridges were activated passing through acetonitrile (5 mL), water (10 mL) and CTABr aqueous solution (0.025 M, 4 mL). Ash aqueous extracts (300 mL) with added acetonitrile (90 mL) were loaded into the conditioned cartridge followed by 10 mL of a water/acetonitrile solution (75:25) used to transfer quantitatively the PAHs in the sample. The cartridge was dried by means of a gentle stream of nitrogen for 20 min, and PAHs were subsequently eluted with 8 mL of a hexane/dichloromethane solution (70:30). The collected solution was taken to dryness by rotary evaporation, and the residue obtained was redissolved in acetonitrile (0.5 mL). The new solution was filtered through nylon membranes (0.45 μm) and 50 μL were injected into the chromatographic system.

RESULTS AND DISCUSSION

Performance of the Extraction of PAHs from Ashes. The ashes with PAHs used for extraction optimization were obtained by ignition and catching fire on *Populus sp*. matches. PAHs extraction from ashes was optimized having into account parameters such as extraction solvent and number of consecutive extractions, sample particle size, and extract cleanup. Different nonpolar solvents used for PAHs extraction from soils (*23*, *24*) were assayed. The decreasing order of recovery performance with ashes was: dichloromethane > ethyl acetate > ethyl acetate/hexane (3:7) > bencene > acetone/hexane (1:2) > hexane. The first extraction with dichloromethane proved to be nearly quantitative because PAHs recoveries were all higher than 80% (81−97%) for the different components; consecutive extractions were then disregarded. With the intention of increasing repeatability, it is important that samples have a small and homogeneous particle size, above all when the sample quantity is low (mg); extraction tests with dichloromethane (10 mL) were then performed after sieving ash samples (0.1 g) at < 0.2 and < 0.5 mm ($n = 4$). Relative standard deviation percentages (RSD%) were 6−11% for the experiments at 0.2 mm, and 13−32% for those at 0.5 mm. Sieving of ash samples at 0.2 mm was then selected. Different polar minicolumns were subsequently tested for extract cleanup: acid, basic, and neutral alumina; diol; amino; florisil; and silica. Dichloromethane, the extraction solvent, was evaporated to dryness and replaced by hexane (10 mL), and the hexane solution loaded into the minicolumns. When 9 mL of hexane were passed through the minicolumns, PAHs were eluted retaining most of the co-extracted interferences in the cartridge, especially in that made of silica. With the proposed method, the PAHs found in the ashes obtained from *Populus sp*. matches and the rest of wood materials were determined (**Table 2**).

Table 2. Content of PAHs in Ashes (Average ± Standard Deviation in μg/kg; $n = 4$) Obtained by Ignition and Firing the Material with a Flame (Match-Like Combustion)[a]

PAHs	*Populus sp.* matches	fired samples			
		Eucalyptus	*Pinus*	*Ulex*	*Erica*
B[*a*]A	258 ± 6	203 ± 34	308 ± 6	468 ± 17	380 ± 13
B[*b*]F	211 ± 11	116 ± 17	499 ± 11	231 ± 4	200 ± 10
B[*k*]F	157 ± 11	84 ± 12	169 ± 11	196 ± 5	177 ± 7
B[*a*]P	274 ± 9	170 ± 25	191 ± 9	414 ± 4	380 ± 9
D[*ah*]A	nq[b]	nq	nq	nq	nq
B[*ghi*]P	213 ± 10	59 ± 7	139 ± 10	156 ± 8	99 ± 7
I[*1,2,3-cd*]P	113 ± 4	58 ± 9	121 ± 5	147 ± 7	118 ± 11
∑PAHs	1226	690	1427	1612	1354

[a] No PAHs were found by heating the same material in an oven. [b] nq, non quantifiable

Table 3. Recoveries ± Repeatabilities, Instrument Linear Dynamic Ranges, Determination Coefficients (r^2) and Limits of Detection (LOD) and Quantification (LOQ) of the Method for Determining PAHs in Wood Ash Samples. The Blank Samples Obtained in an Oven Were Fortified with PAHs for Such a Study

PAHs	absolute[a] recovery			standards linearity[b]		LOD[a]	LOQ[a]
	(μg/kg)	%	±RSD	range (μg/L)	r^2	(μg/kg)	(μg/kg)
B[*a*]A	97	91	4	2–65	0.9996	0.7	1.5
B[*b*]F	180	97	4	4–130	0.9994	2.2	5.6
B[*k*]F	121	95	3	2–65	0.9995	0.3	0.8
B[*a*]P	175	92	3	4–120	0.9992	1.2	3.2
D[*ah*]A	176	82	3	4–120	0.9994	1.9	5.2
B[*ghi*]P	232	81	6	5–175	0.9991	0.2	0.7
I[*1,2,3-cd*]P	170	86	3	4–120	0.9991	0.3	0.8

[a] ($n = 4$). [b] ($n = 12$; 6 levels in duplicate) determinations.

There are not any ashes as Standard Reference Material (SRM) with certified contents of PAHs to be able to characterize the proposed method; SRM 1649a, urban dust, an atmospheric particulate material collected in an urban area with certified PAHs contents by the National Institute of Standards and Technology, was considered very different to the ashes studied. Because a single extraction with dichloromethane fully recover all PAHs in nonspiked ashes (obtained by match-like combustion), method characterization was performed with PAH-spiked ash samples (obtained by oven combustion). An *Erica cinerea* sample of wood ash with no PAHs, obtained by heating at 300 °C for 15 min and limiting air input, was then fortified with all PAHs, and the spiked sample was analyzed after being left overnight protected from light under refrigeration conditions; the results are summarized in **Table 3**; all recoveries percentages were higher than 80%, while RSDs% were lower than 6%. There were no matrix effects affecting results when spiked ash samples were analyzed according to the proposed procedure, because the results obtained with spiked *Erica* ashes were not statistically significantly different from those obtained by repeating the procedure with the other different spiked ashes at the 95% probability level. Limits of detection (LOD) and quantitation (LOQ) were evaluated on the basis of the noise obtained with

Table 4. Consecutive Extractions of PAHs from *Populus sp.* Matches Ash into Waters (ng/L; $n = 2$)[a]

PAHs	1st extraction	2nd extraction	3rd extraction
B[*b*]F	2.5	2.8	3.7
B[*k*]F	2.0	1.9	0.9
B[*a*]P	2.0	3.7	2.8
B[*ghi*]P	nd[b]	4.6	3.0
I[*1,2,3-cd*]P	nd	nd	nd
∑PAHs	6.5	13.0	10.4

[a] Only those pahs indicators of drinking water quality were selected. [b] nd, non detectable.

the analysis of unfortified oven ash samples ($n = 4$). LOD and LOQ were defined as the concentration of the analyte that produced a signal-to-noise ratio of 3 and 10, respectively (*25*) and were then tested experimentally by spiking blank samples at such levels.

Content of PAHs in Ashes and Release into Water. The method was applied to four different ash samples obtained by ignition and firing the material with a flame (match-like combustion); two were from trees and two from bushes (**Table 2**). Overall PAHs values (∑PAHs) were between 690 and 1612 μg/kg, depending on the material (*Pinus* > *Eucalyptus*; and *Ulex* > *Erica*). For the ashes obtained by heating these materials in an oven at 300 °C for 15 min and limiting the oxygen input, no PAHs were found at quantifiable levels.

Blank ash aqueous extracts, obtained by mixing 0.3 g *Erica* oven ashes with 300 mL of water, were spiked with all PAHs. The fortified aqueous extracts were shaken by magnetic stirring in amber glass vials to protect waters from light and keeping constant water temperature at 12 ± 2 °C. PAHs resulted, therefore, to be stable at any pH (pHs 4, 7, and 10 were tested) for at least 1 h. With the intention of monitoring the transfer of PAHs from ashes to water, *Populus* fired match ashes (0.3 g) were consecutively extracted with water (300 mL). The levels obtained after 15 min shaking at 12 ± 2 °C during three consecutive extractions are shown in **Table 4**. The PAHs levels transferred to waters were very low due to their poor solubility in water and well below the maximum permitted levels for surface waters (<0.2 or 1 μg/L) (*26*). Overall extracted percentages (∑PAHs) were 0.7, 1.3, and 1.1% consecutively. Ashes can be therefore considered as stable PAHs reservoirs for long, which continuously release low levels of PAHs to runoff waters.

Conclusions. As far as we know, there are no published methods to determine PAHs in ashes obtained from plant materials; the reason perhaps is the difficulty of such a determination. The proposed method helps to cover some of the most important research and development needs in the area of PAHs fate from ashes to assess the state of the aqueous environment with respects to PAHs. The method resulted to be of high recoveries (ranging from 81 to 97% for the different PAHs), with repeatabilities (RSDs%) better than 6%. Detection levels were from 0.2 to 2.2 μg/kg, while quantification limits were from 0.7 to 5.6 μg/kg, low enough to evaluate the presence of PAHs in wood ashes. These method characteristics allow calibration by direct injection of PAHs standards solutions into the head of the column, which always makes the analytical work easier. The linearity range was from 2 to 175 μg/L ($r^2 > 0.9991$).

The kind of combustion performed on vegetal material seriously affected the PAHs levels in ashes, because ignition and firing the material with a flame (match-like combustion) versus heating in an oven are the processes that produce PAHs in the ashes. At water temperatures of 12 °C, the percentage of PAHs transferred from ashes to water keeps constant around 1% in any of three consecutive extractions. Although PAHs concentrations in waters will keep below legal limits for surface waters, PAHs contents in waters surrounding fired areas should be carefully studied to prevent contamination risks.

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