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Organic pollutants profiling of wood ashes from biomass power plants linked to the ash characteristics



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HIGHLIGHTS

- The sum of BTEX + S varied from nondetected to 30 mg/kg.
- Total amounts of PAHs (total PAHs) ranged between non-detected to 422 µg/kg.
- The larger T50 (with more burned organic matter), the higher BTEX + S levels.
- The higher the QMO (or lower combustion), the higher presence of PAHs.
- The ashes are suitable for soil applications, as an organic amendment.

GRAPHICAL ABSTRACT



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ABSTRACT

Purpose: Wood ash, characterized by high content of certain nutrients and charcoal, can be applied to soils as a means of managing this waste product improving the soil quality. The associated environmental risk must be assessed. The objective of this study was to characterize the bottom and fly ash collected from 15 biomass power plants in Spain by determining the benzene, toluene, ethylbenzene, xylene and styrene (BTEX + S), PAHs and aliphatic hydrocarbon contents of both types of ash. Biochar was also used for comparison purposes. *Methods:* Gas chromatography–mass spectrometric methods were used for the identification and determination of both BTEX + S and aliphatic hydrocarbon contents in bottom and fly ashes, as well as biochar. High performance liquid chromatography with fluorescence detection was used for PAHs measurements. Multivariate correlation analysis was used to determine the relationship between sample characteristics and pollutants identified by partial least squares regression analysis.

Results and discussion: In general, the degree to which organic matter in the sample is burned increases with T50 or the "50% burn off" temperature (possibly due to the addition of fuel), and the BTEX + S also tended to increase. However, as the Q/MO (the heat of combustion divided by organic matter mass) increased, the combustion decreased or proceeded with less oxygen, which appears to be related to an increased presence of PAHs. The results confirm that the amounts of organic pollutants (PAHs and BTEX + S, together with total aliphatic hydrocarbons)

* Corresponding author at: Nutrition and Bromatology Group, Department of Analytical and Food Chemistry, Food Science and Technology Faculty, University of Vigo, Spain. *E-mail address:* jsimal@uvigo.es (J. Simal-Gándara). in the wood ash do not exceed limits established for different soil or industrial uses. *Conclusions:* Both types of ash, together with biochar, may therefore be suitable for application to soil as a fertilizer and an organic amendment, taking into account the target organic pollutants.

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1. Introduction

The wood ash generated in biomass power plants contains high levels of nutrients and charcoal and can be applied to soils (Augusto et al., 2008; Omil et al., 2013). These studies showed that application of wood ash to land increased the soil pH and nutrient levels. In addition, because the significant content in charcoal, this practice may also help to improve the SOM content, enhance soil microbiology activity and enhance the C stocks of degraded agricultural soils. Incineration greatly reduces the volume of the waste disposed (Danish Energy Agency, 2012). Fly and bottom ashes are the main by-products from the combustion of solid biomass, representing 5.0% and up to 30% of initial weight of waste, respectively (Lapa et al., 2002). Fly powdered ash, suspended in the flue gases, is the finest part and is typically light grey. Fly ash represents up to 40% of the total ash. Bottom ash (or mixed wood ash), which settles under the grate of the combustion chamber, is the coarsest component of the combustion by-products. Bottom ash is generated in wood fired furnaces and contains significant amounts of charcoal (Melotti et al., 2013; Santalla et al., 2011).

Large volumes of plant residues are burned in industrial power plants, at a combustion temperature from 500 to 800 °C, under oxic conditions. The concentrations of PAHs in wood ash vary depending on the boiler operating conditions and on differences in the origin and composition of biomass (Pérez-Gregorio et al., 2010; Rey-Salgueiro et al., 2004) and could range from 15 to 733 µg/kg (Straka and Havelcová, 2012). Nevertheless, the organic compounds possibly present are not usually addressed and in these kinds of samples, it is important to know not only the inorganic but also the organic toxic substances (Straka and Havelcová, 2012). Sixteen PAHs are listed as priority pollutants by the United States Environmental Protection Agency (USEPA, 2013). Benzene, toluene, ethylbenzene, the ortho, para and meta xylenes (BTEX) and styrene (S) are petroleum-derived volatile organic compounds, and can occur in wood ash. BTEX has been adopted by state agencies as an "indicator" from petroleum products. Combustion of agricultural residue-derived fuels leads to BTEX emissions (Galbally et al., 2009; Krugly et al., 2014; Sinha et al., 2006). They can also remain in the combustion residue. Most previous research has focused on PAHs in fly ash (Masto et al., 2015; Straka and Havelcová, 2012), and very few have characterized organic pollutants in bottom ash from biomass power stations.

Biochar is generated by biomass pyrolysis at temperatures ranging from 350 °C to 1000 °C, in oxygen-limited conditions (unlike bottom and fly ash). Feedstock for biochar production may comprise purposegrown biomass or waste material from forestry or agriculture, guaranteeing compliance with all environmental threshold values and declaring all product properties for its agricultural use (European Biochar Certificate, 2012). Biochar may also become contaminated with PAHs or BTEX during pyrolysis (Brown et al., 2006; Fabbri et al., 2012; Hale et al., 2012; Nakajima et al., 2007).

The objective of the current study was to obtain basic information about concentrations of PAHs, total petroleum hydrocarbon (TPH), BTEX and S in bottom and fly ash produced in different industrial power plants in which different combustion systems are used. Commercial biochar samples were also analysed and used as reference samples for comparison. The relationship between pollutant variables and indices of the samples was also considered.

2. Materials and methods

2.1. Sampling design

Ash samples were collected from 15 biomass power stations in Spain. Pine and eucalyptus branches and bark were used as the main types of feedstock in the power plants. However, in some of them waste wood was also employed.

For this study three types of burnt plant biomass were selected:

- a) Fly wood ash (FWA): Nine samples of FWA were collected from Circulating Fluidized Bed (CFB) boilers. The feedstock of this type of WA was eucalyptus branches, which were burnt at temperature of 750 to 900 °C.
- b) Mixed wood ash (MWA): 18 samples obtained in conventional grate-fired combustion boilers and 9 samples obtained in water-tube boilers. The feedstock of this type of WA was pine branches (18) and waste wood (9), which were burnt at temperature of 400 to 500 °C. Since MWA samples were very heterogeneous, in order to know if composition was dependent on the particle size/granulometry, MWA samples were fractionated in three fractions: <2 mm, 2–5 mm and >5 mm.

All wood ash samples were collected by the following procedure, to ensure that they were representative of the ash produced. Thus, about 2.0 kg of ash was collected three times a day during one week and these subsamples were mixed thoroughly.

c) Five commercial biochar samples (pine branches) were also analysed for comparative purposes. They were pyrolyzed at 600 °C for 5 h. Each fraction was weighed and characterized to determine the organic matter content and quality, PAHs, TPH and 9. For each determination, three replicates were analysed per sample.

2.2. Characterization of the organic matter in wood ash

Samples of wood ash were dried at 40 °C to constant weight. All samples were ground to a powder. The organic matter (OM) content of the wood ash was calculated by loss-on-ignition (LOI), as follows:

LOI (%) = ((Weight_{105} - Weight_{600}) / Weight_{105}) × 100

where Weight₁₀₅ is the weight of samples after heating at 105 °C and Weight₆₀₀ is the weight of sample after ignition at 600 °C. To obtain information about the molecular characteristics of the charred material, the samples were milled and analysed by differential scanning calorimetry (DSC). The DSC experiments were performed under dry air at a flow rate of 2.1 kg/cm² and a scanning rate of 10 °C/min, with ash samples (10 mg) placed in open pans. The temperature range was 50-600 °C. Samples of indium (mp: 157 °C) were used to calibrate the calorimeter. The "50% burn off" temperature (T50) (Leifeld, 2007) was determined as the temperature at which the weight loss of a sample reached the half of the overall weight loss due to oxidative decomposition in the temperature range 200–550 °C. The heat of combustion (Q, in J/g) was determined by integrating the DSC curves over the exothermic region (150-600 °C). Data recorded at <150 °C were discarded, thus obviating weight losses and energy changes associated with moisture loss. The Q values were divided by the mass loss (both measured between Download English Version:

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