



PAHs and potentially toxic elements in the fly ash and bed ash of biomass fired power plants



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ABSTRACT

PAHs and heavy metal chemical fractions were determined in biomass ashes from four power plants that fired coconut, chicken, and wood wastes. All these ashes were alkaline (pH 8.7–12.7). High unburned carbon in the fly ashes (8.3 to 16.9%) indicates incomplete combustion. The major chemical phases were SiO_2 – CaO – K_2O – MgO followed by $\text{Fe}_2\text{O}_3 > \text{Al}_2\text{O}_3 > \text{SO}_3 > \text{MnO}$, with an exception of higher P_2O_5 (5 – 8.8%) in chicken litter ash. SEM showed that the FAs have more angular particles, whereas BAs have fused and glassy particles. The contents of B (15– 205 mg/kg), Cu (236 – 481 mg/kg), Cd (13 – 23.2 mg/kg), Ni (50 – 186 mg/kg), and Zn (10 – 400 mg/kg) were relatively higher in the ashes. Most of these elements (except B) were associated with metal oxide and silicates. B is the most mobile element and >75% of B is present in the available forms. The total PAH content was comparatively lower (0.19 – 12.3 mg/kg), except for wood ash (PAH 193 mg/kg). These ashes have significant amount of plant nutrients and most of the potentially toxic elements are in non-available forms which supports their suitability for soil amendment.

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1. Introduction

Bioenergy is the largest source of renewable energy today and can provide heat, electricity, as well as transport fuels [1]. Though coal is already the leading resource for power generation, followed by wind and hydel-power generation, the biomass generated in the form of solid waste like wood chips, vegetable wastes, slaughter house waste, firewood, agricultural wastes, crop stalks, agro residues etc. are also used for power generation and thermal applications. Electricity supply from bioenergy has been rising steadily since 2000; in 2010 bioenergy provided some 280 TWh of electricity globally, equivalent to 1.5% of world electricity production [1]. The combustion of biomass is steadily increasing worldwide, but only few studies have been conducted on environmental assessment of biomass ash. The ash generated from burning of the biomass may pose threat to the environment due to the presence of potentially toxic elements and polycyclic aromatic hydrocarbons (PAHs).

Biomass ashes are often characterized for heavy metals, but the organic compounds are not usually addressed. Recent studies demonstrate the presence of PAHs in wood ash at varying concentrations [2].

In biomass combustion, polycyclic aromatic hydrocarbons (PAHs) are created by secondary aromatization reactions in char in the pyrolysis phase of incomplete biomass combustion at temperatures higher than 400 °C [3]. Anthracene, fluoranthene, pyrene, benzo[a]anthracene and chrysene are predominant PAHs emitted from combustion of biomass fuels [4]. The concentrations of Σ PAHs in both gas and particle phases varied from 1.3 to 1631.7 $\mu\text{g}/\text{m}^3$ for a wood chip fired boiler. The species of tree was less important than the boiler operating conditions in affecting PAH concentrations [5]. In a wood pellet based boiler, >80% of the PAHs was emitted in the gas phase. PAHs in the gas phase comprised mainly of low molecular mass compounds, while PAHs in the particulate phase (ash) were mostly composed of high molecular mass compounds [6]. The total PAH content in a wood and straw based biomass ash varied in the range of 15–733 $\mu\text{g}/\text{kg}$ [7]. A study of bottom ash from medical waste incineration showed that the total PAH ranged from 162 to 3480 $\mu\text{g}/\text{kg}$ [8], and in another clinical waste incinerator, the sum of the amounts of 11 PAHs was found to be 449.3 $\mu\text{g}/\text{kg}$ [9]. The data on PAH content in biomass ash is very limited.

Like PAHs, the heavy metals in biomass ash have got immense environmental issues and their concentrations are also highly variable due to the difference in origin and composition of biomass species. Concentrations of some trace elements (Ag, Au, B, Be, Cd, Cr, Cu, Ni, Rb, Se, Zn, etc.) in biomass ash can be very high due to the enhanced enrichment of such elements in the combustion residue due to the high contents of organic matter in biomass [10]. Among the different wood ashes, the toxic elements like As (1.97–5.19 mg/kg), Cd (0.839–1.214 mg/kg), Cr (2.56–4.58 mg/kg), Cu (29.3–43.0 mg/kg), Pb (28.38–35.04 mg/kg), and

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Hg (0.064–0.108 mg/kg) were observed in the beech and *Ailanthus* trunk wood [11]. Birch wood ash contains very high concentrations of Pb (1.3%), Zn (4.4%) and Cd (203 mg/kg) [12]. The order of concentration of elements in the biomass ashes (wheat straw, olive bagasse and hazelnut shells) from the highest to the lowest values was as follows: Fe > Mn > Zn > Cu > Ni > Cr > Pb > Co [13]. Singh et al. [14] observed high content of Cr (61 mg/kg), Cu (113 mg/kg), Pb (26 mg/kg) and Zn (167 mg/kg).

In a review on wood ash, Pitman [15] found that Zn, Ni and Cu in bottom ash can pose the risk of exceeding permissible levels if the ash is applied to soil in large quantities, but Cr, Cd, As, Hg and Pb contents cause no risk. Studies on bottom ash obtained from three types of bioenergy systems — a fixed-bed boiler, a downdraft gasifier and a wood pellet boiler showed that the trace element contents of the biomass ashes were all within the environmental limits for soil amendments in British Columbia, Canada [16]. Leaching study with biomass (eucalyptus and pine) ash revealed low or undetectable concentrations of heavy metals and metalloids in the eluate, showing low mobility of these metals [17]. Leaching of the trace elements is sensitive to the pH of the ash [18], most of the biomass ashes being alkaline may enhance the release of oxyanionic-forming species of As, B, Cr, F, Mo, Sb, Se, V and W [19]. The leaching tests are only simulations of the practical situation and may not reflect the actual leaching level of ash in real environments. Moreover, lower leaching levels do not ensure safety [20].

Vassilev et al. [10] expressed concern about the unfavorable modes of occurrence and release of potentially toxic elements from biomass ash which could be an environmental challenge. Unfortunately, there are numerous indications that dangerous trace elements such as As, Bi, Br, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, V and Zn are present in water-soluble phases in biomass ash [19]. Thus the assessment of the chemical forms of the metals will help to determine the bioavailability, mobility and toxicity of the biomass ash. Systematic studies on the modes of occurrence, behavior and fate of hazardous phases and trace elements in biomass ash are at juvenile stage [19].

In view of the limited information on the heavy metal chemical fractionation and PAH content in the biomass ash, the present study was aimed to determine the fractions of potentially toxic elements and PAHs in the fly ash and bottom ash of biomass fired power plants.

2. Materials and method

2.1. Sampling

Fly ash and bottom ash samples were obtained from 4 different biomass based power plants located in Tamil Nadu, India. These biomass power plants (BP) use variety of mixed feeds like rice husk, sugarcane bagasse, municipal solid waste, paper and chicken wastes, coconut husks, *Prosopis juliflora* chips, match stick and match box wastes, pencil wastes, etc. The plant capacity and the most prominent feed are listed as follows: BP-1 (10 MW; coconut and chicken waste); BP-2 (7.5 MW; coconut waste and *Prosopis* bioenergy tree chips), BP-3 (7.5 MW; coconut and chicken waste and *Prosopis* chips), BP-4 (18 MW; *Prosopis* chips and wood waste). These biomasses were fired in a traveling grate furnace at around 850 °C with 40–50% excess air. The feed size was about 20 mm. The fly ash samples were collected from the hopper fixed below the electrostatic precipitators and the bottom ash was collected from tank below the grate. Five samples were collected from each plant and the mean data are presented. Initially all the samples were stored at 4 °C. Before analysis the samples were dried at 105 °C in a hot air oven and ground (Retsch — Mortar Grinder RM 200) and passed through 100 mesh sieve.

2.2. Sample analysis

Electrical conductivity and pH of the biomass ash samples were measured with a solid to liquid ratio of 1:2.5 [21]. Unburned carbon was determined by following the ASTM method 7348-13 [22]. The chloride content was determined in the water extract of these ashes by silver nitrate titration method [23]. The major and minor elements present in the ash were analyzed by ASTM method D6349-13 [24]. The sequential extraction of potentially toxic heavy metals was adopted from Van Herck and Vandecasteele [25], and the following fractions of metals were extracted.

- (i) Water soluble fraction (metal salts that are easily soluble): 5 g of ash sample was taken in polyethylene bottles and shaken with 50 ml pure Millipore water for 3 h at room temperature. The solution was filtered using Whatmann filter paper 42, the filtrate was kept for heavy metal analysis.
- (ii) Exchangeable fraction (metals bound to surface sites): the residue from the previous step was treated with 8 ml 1 M MgCl₂ and shaken for 1 h at room temperature and filtered.
- (iii) Carbonate bound fraction (metals that are released as acid soluble salts): the residue from the previous step was shaken with 50 ml 1 M sodium acetate (CH₃COONa, pH 5) for 1 h at room temperature and filtered.
- (iv) Metal oxide bound (metals encapsulated in iron and manganese oxides): the residue obtained from the previous step was treated with 50 ml 0.04 M hydroxylamine hydrochloride (NH₂OH·HCl) in 25% acetic acid (CH₃COOH) and digested for 5 h on a hot plate at 96 °C. After digestion the solution was filtered.
- (v) Organic bound (metals that are organically bound or oxidizable minerals like sulfides): the residue from the previous step was treated with 10 ml 30% H₂O₂ and 10 ml 0.02 M HNO₃ were heated at 85 °C for 3 h, covered with a watch glass and digested for 1 h. After the solution got vaporized the residue was cooled and 20 ml 3.2 M CH₃COONH₄ in 20% HNO₃ was added and agitated continuously for 30 min and the solution were filtered.
- (vi) Residue fraction (metals that are encapsulated in the silicate structure of the ash): 0.2 g the residue was subjected to microwave digestion with 7 ml HNO₃, 3 ml HCl and 2 ml HF for 30 min at 220 °C.

The above digested and extracted solutions were analyzed for heavy metal contents by ICP-OES (ICAP 6300Duo, Thermo Fisher Scientific, UK). All elements (except As) were measured using the normal cyclonic spray chamber and concentric nebulizer connected by tygon tubings. Determination of As was carried out using ICP-OES with an online hydride accessory. For elemental analysis (except As), the ICP was set with a RF power of 1150 W and a pump speed of 50 rpm, plasma gas flow at 12 l/min, and the nebulizer gas flow at 0.5 l/min. For As analysis, the RF power was reduced to 1100 W and pump speed reduced to 45 rpm. Milli Q double distilled water was used for the preparation of reagents, standards and samples. All glassware were washed with Extran (Merck), followed by tap water, then by 20% (v/v) nitric acid and finally rinsed with double-distilled water. Multi elemental standard solution (CertiPUR) (1000 mg/l) procured from Merck, Germany was used for the development of calibration curves. Yttrium was used as internal standard for consistency in sample measurement. NIST coal fly ash (NIST 2689) certified reference material (CRM) was used for quality assurance. The percent recovery of elements from NIST 2689 CRM ranged from 98.8% for Ni to 118% for As. The blank reagent and standard reference material were analyzed intermittently, to verify the accuracy and precision of the digestion procedure. After every tenth sample during analysis, the calibration standards were analyzed to check the analytical accuracy. The analytical variations of these repeated standard samples were within 5%. Method detection limits (MDLs) were

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