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Bottom ash of trees from Cameroon as fertilizer

Christoph Maschowski [a,*], Marie Claudine Zangna [b], Gwenaëlle Trouvé [c], Reto Gieré [d]

[a] *Institut für Geo und Umweltnaturwissenschaften, Albert-Ludwigs-Universität, 79104 Freiburg, Germany*
[b] *ACK – Alumni Club Kamerun, Yaoundé, Cameroon*
[c] *Laboratoire Gestion des Risques et Environnement, Université de Haute-Alsace, 68093 Mulhouse Cedex, France*
[d] *Department of Earth and Environmental Science, University of Pennsylvania, Philadelphia, PA 19104-6316, USA*

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ABSTRACT

Utilization of wood bottom ash as fertilizer additive contributes to the return of valuable nutrients to agricultural soils, especially when no artificial mineral fertilizer is being used. In general, wood combustion ash is enriched in calcium and potash, and may also contain elevated amounts of zinc, but the concentrations of these elements depend on tree species, part of the tree, harvest season and local soil type. In this study, bottom ash samples from eight different agricultural wood species from Cameroon, Africa were investigated by using X-ray diffraction and atomic absorption spectroscopy to determine the refractory components and the concentrations of selected heavy metals and arsenic. Results show calcite, potassium salts, periclase and quartz as major components. These phase contents were used to calculate major element concentrations, which were subsequently validated by X-ray-fluorescence analysis. The chemical compositions varied within the range of common compositions of wood ashes. Six of the ashes reached sufficient concentrations of calcium to be defined as a "calcium fertilizer". Pb contents are most variable, ranging from 0.03 to 21.1 mg/kg. Concentrations of Ni, Cu, Zn, Cd, Pb, and As are all lower than the strictest limit concentrations required for wood ash fertilizers and therefore, the studied wood ashes can be used without environmental concern.

1. Introduction

Solid biomass, e.g. wood, contains various inorganic components in different amounts and speciation, depending on plant type, plant part, soil, and harvest season (Vassilev et al., 2010). Inorganic constituents remain as ash after combustion, as they are non-combustible. Depending on the level of completeness of the combustion, the ash may contain some organic compounds (Vassilev and Vassileva, 1997). The ash is separated into two fractions: one remains on or below the combustion grate as bottom ash; the other is transported along with the flue gas as fly ash, and it comprises the minor part in open fireplaces. Bottom ashes are considered to be unproblematic and sometimes are used as fertilizer additives, because they contain valuable nutrients (Röser, 2008). Fly ashes, however, may be enriched in (toxic) heavy metals and metalloids and therefore, have to be disposed as problematic waste, after being trapped by a flue gas treatment device. The suitability of bottom ashes for utilization as fertilizer additive/soil amendment strongly depends on fuel type and soil quality, and has to be assessed for each species and locality (Vassilev et al., 2013a,b). Therefore, the characterization of a wide range of biomass ash types can help in understanding the nutrient cycle and trace element uptake processes, especially when it is crucial to return ashes from biomass combustion to the soil in order to avoid depletion of nutrients.

Within the living memory, potash is known as vital nutrient for plant growth, as it consists essentially of water-soluble potassium-bearing salts, which are completely bioavailable (Sharifi et al., 2013). Because the potassium content in wood ash can be as high as 50% by weight (calculated as K_2O), this type of ash is being used as a source of potassium for the production of fertilizers, glass (Tite et al., 2006) and soap (Farmer, 2013). However, in modern agriculture, ash from wood combustion is no longer considered a feasible source of potassium, but wood ash might be the only potassium source, when no artificial/mineral fertilizer is used and the soil type is depleted in this element, e.g. when no clay-minerals are present (Barre et al., 2007).

Ash from wood combustion is depleted in nitrogen and therefore, cannot be used as a general fertilizer (Röser, 2008), but can be

* Corresponding author.
E-mail address: christoph@maschowski.de (C. Maschowski).

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taken as a special amendment to deliver alkaline earth metals, which are able to neutralize acidification of the soil caused by acid rain, i.e. atmospheric pollution (Clarholm, 1994). In general, the calcium concentrations in wood ash are relatively high (Ca mostly present in the form of calcium carbonate and/or calcium oxide), and therefore, wood ash may be used as liming agent to neutralize acid soils and increase the activity of soil bacteria (Bache and Sharp, 1976). In addition, some wood ash types contain enough sulfur and phosphorous that they could be considered as a source of these macro-nutrients.

In this study, samples of wood bottom ash from eight different agricultural tree types from Cameroon were investigated by using X-ray diffraction (XRD) with subsequent Rietveld refinement, and by X-ray fluorescence (XRF) and atomic absorption spectroscopy (AAS). The main goals of this study were to identify the crystalline phases and their relative proportions, to evaluate the suitability of combining different analytical techniques, and to compare the concentrations of some troublesome heavy metals and arsenic against strictest limit values for wood ash and other mineral fertilizers (Anon., 2002) (Vesterinen, 2003) in order to find out whether or not the ashes could be used as fertilizers in Cameroon.

2. Samples and methods

All trees were harvested in January 2011 in the bush-region of the village Evondo near the international airport ‘Nsimalen’ of Yaoundé, Cameroon (geo-coordinates: 3.743300, 11.524313). To represent a real-life scenario, the wood specimens consisted of a mixture of different tree parts (stem wood with bark and twigs). All tree samples were stored for one year prior to combustion for drying reasons. The soil in this region is classified as a “Ferralsol” according to the Harmonized World Soil Database (IIASA, 2012), which stands for iron- and aluminum-rich soil types, often depleted in nutrients. The geological basement underlying the soil consists of metamorphic rocks, represented by embrechite (metamorphic migmatite) and gneiss (Geological map of Cameroon (BMArchives, 2015)).

The ash samples studied here were produced by combustion in open fireplaces of eight tree species (Fig. 1), which were burned in the vicinity of Yaoundé, Cameroon. The ashes represent bottom ash and were collected directly after combustion, following cooling. All ash samples were ground in an agate mortar and analyzed by XRD with a Cu-Kα X-ray source, using a high-precision setting (2–75°2θ; step size of 0.005°; 5s/step) on a BRUKER D8 Advance diffractometer at the University of Freiburg, Germany. The raw data were processed with pattern matching software (BRUKER DIFFRAC.EVA) in order to identify the phases present (Fig. 2). For each of the identified phases, a structure file was obtained from the American Mineralogist Crystal Structure Database (Downs and Hall-Wallace, 2003). These structure files were then applied to the datasets in the Rietveld refinement program DIFFRACsuite TOPAS by Bruker ltd. to determine the relative proportions of crystalline phases present (Fig. 3). The amorphous content was determined from background signal (Scarlett and Madsen, 2006).

Quality of the data retrieved from XRD and Rietveld refinement depends on various aspects: sample preparation (grain-size distribution, surface roughness), degree of crystallinity (amorphous content, e.g. glassy substances and organic matter), and strategy of the refinement procedure (e.g. (Ward and French, 2006)).

Grain-size of the sample depends on the preparation method. In our case, we ground it manually with the help of an agate mortar, which is a working practice, but not as accurate as automated grinding. Surface roughness depends on the technique of distributing the sample into the mold of the sample holder, which was done manually as well.

Quantification of the amorphous content is usually achieved by spiking the sample with a specific concentration of a known substance, which is 100 percent crystalline. From this information, Rietveld refinement software tools can easily define the degree of crystallinity of the sample. Because of limited sample quantity, we decided to perform XRD measurements without spiking the sample, so that enough uncontaminated material was kept for subsequent XRF and AAS analyses. The calculation of the amorphous content, however, is important; in our case it was done by adding an artificial one-peak phase representing the background signal and thus the amorphous part of the sample. The uncertainty of this method cannot be determined, but the applied method seems to work quite well for the ashes of this study.

The refinement procedures were performed without comprehensive corrections like the compensation of preferred orientation, lattice parameters and micro-strain.

The bulk chemical composition of the ash samples was analyzed by SGS Lakefield, a Canadian laboratory with ISO17025 standard specializing in geochemical analysis. The specific XRF-analysis method used for this project was the BORATE FUSION/XRF WHOLE ROCK PACKAGE (GO XRF76V).

To obtain accurate data for selected heavy metals and arsenic, the samples were also analyzed by AAS at the University of Freiburg, Germany, using an AAS Vario 6 instrument with graphite tube by Analytik Jena. The samples were first digested with a mixture of nitric acid and hydrochloric acid (aqua regia) under microwave treatment.

3. Results

The macroscopic colors of the ashes are relatively light for all tree types (see photographs in Fig. 1). The color descriptions given in Fig. 1 conform to the RAL color matching system used in Europe. The light color reflects the presence of only small amounts of organic matter residue, i.e. the combustion process was quite complete. Therefore, the carbon content was not determined and will not be discussed further in this study.

3.1. Mineralogical composition

All ash samples contain a considerable amount of calcite (*$CaCO_3$*), ranging from 25.8 to 70.7 wt% (percent by weight = $g \cdot 100\,g^{-1}$) (Table 1, Fig. 4). They are further characterized by relatively low contents of arcanite (*K_2SO_4*), which ranges from 4.17 wt% (mango tree) to 9.26 wt% (cheesewood). Other potassium phases identified include a chloride (sylvite) and a K-bearing carbonate (fairchildite), which is the most variable component, ranging from undetectable amounts (abachi tree) to 38.8 wt% (African drupe tree). The concentration of free lime (*CaO*) is unexpectedly low (≤4.42 wt%); in the ashes produced through combustion of avocado tree and African tulip tree the phase was not even detected by XRD (Table 1). Periclase (*MgO*) is the only magnesium phase present, and its concentration may be as high as 13.1 wt% (African tulip tree). Similarly, halite (*NaCl*) is the only sodium-bearing phase, but its concentration is very low, except for the ash derived from the abachi tree (12.3 wt%). The content of quartz (*SiO_2*) is highly variable among the different samples (1.67–21.7 wt%), as is the content of amorphous material (7.49–41.4 wt%).

3.2. Bulk chemical composition

3.2.1. Oxide concentrations derived from XRD data

In order to assess the utilization potential and quality of the ashes as fertilizer additives, the concentrations of all phases