

## CHARACTERIZATION OF FLY ASH FROM THE GASIFICATION OF WOOD AND ASSESSMENT FOR ITS APPLICATION AS A SOIL AMENDMENT

Hui Pan<sup>a,\*</sup> and Thomas L. Eberhardt<sup>b</sup>

Fly ash was collected as a byproduct from the processing of southern pine wood chips in a pilot-scale biomass gasifier. General properties of the fly ash were determined to assess its applicability as a soil amendment. Its alkaline pH (9.5) and high concentrations of Ca, K, and Mg suggest that it could be used as both a liming agent and a fertilizer. The concentrations of most heavy metals in all ash samples in this study were lower than the ecological soil screening levels used as a guideline. A sequential extraction analysis was used to evaluate the bioavailability of selected nutrient elements and pollutant heavy metals in the fly ash. Most nutrient elements were present in exchangeable/acid extractable and easily reducible fractions. The heavy metals were generally less bioavailable, thus ameliorating concerns for land application of fly ash, with or without prior combustion. Comparison of sequential extraction test results for all of the ashes indicated that the conditions experienced during gasification, such as high processing temperatures, impacted both the total heavy metal concentrations and their potential bioavailabilities.

*Keywords:* Ash recycling; Biomass; Sequential extraction; Bioavailability; Heavy metals

*Contact information:* a: Calhoun Research Station, Louisiana State University Agricultural Center, 321 Hwy 80E, Calhoun, LA 71225 USA; b: USDA Forest Service, Southern Research Station, 2500 Shreveport Hwy, Pineville, LA 71360 USA: \*Corresponding author: Hpan@agcenter.lsu.edu

### INTRODUCTION

Gasification has received considerable attention for the conversion of biomass into synthesis gas, which can then be used directly as an internal combustion engine fuel or converted to liquid transportation fuels by various processes, especially Fischer-Tropsch synthesis (Kumar et al. 2009; Unruh et al. 2010). With respect to the former, equipment (some being commercially available) can convert biomass to electricity by coupling a gasifier with an internal combustion engine equipped with a generator (De Bari et al. 2000; Liao et al. 2007; Kramreiter et al. 2008; Vervaeke et al. 2006). Small-scale gasification-based power plants are of particular interest as means to produce electricity on demand for remote facilities or to provide portable supplies of electricity following power disruptions. Moreover, the opportunity to use locally available biomass resources is highly desirable in that savings can be reaped in lower costs for fuel transportation and the possibility of using biomass resources having little or no commercial value.

The solid byproducts that can be obtained from the thermochemical processing of biomass (e.g., gasification and pyrolysis) are generally a mixture of char and ash, and

often designated as “biochar” when used as a soil amendment (Brewer et al. 2009). Whereas the ash typically recovered from biomass combustion is mostly inorganic, that from biomass gasification can have unburned carbon contents ranging from 10 to 60% (Leiva et al. 2007) analogous to carbon-rich fly ashes generated at coal-based power plants (Yang and Hlavacek 1999). Use of the terms “char” or “ash” alone can be confusing in that they could be construed to mean that the biomass-derived gasifier byproduct may be primarily carbonaceous or inorganic, respectively; the term “char ash” was initially used to describe the byproduct obtained from the gasification of wood, being comprised of nearly equal amounts of char and ash (Eberhardt et al. 2011). Given that said byproduct is carried along by the draft through the gasifier, the term fly ash is appropriate and thus here said byproduct is referred to as (gasification) fly ash.

Traditionally, 90% of the mostly inorganic wood ash derived from paper industry waste and power generation in the US is sent to a landfill (Pitman 2006). The cost of waste disposal has increased due to more restrictive environmental regulations. Development of sustainable and economically feasible methods for fly ash management is therefore of interest to avoid a similar burden to the pending installations of biomass gasification plants. If the fly ash could be used instead of being sent for disposal, the economic viability and public acceptance of biomass gasification as an alternative energy source would be more favorable (Mozaffari et al. 2002).

Application to agricultural or forest soils has been studied as one of the more feasible options for utilizing biomass-derived combustion ashes. Recognizing that the fly ashes now being generated by biomass-based power plants are comprised of both char and inorganic ash components, identifying options for utilization are of recent interest. Whereas a pyrolysis biochar, with its high carbon content, may provide soil stabilization and an opportunity to sequester carbon (Chan et al. 2008), wood ash obtained by combustion, with its high inorganic content, may be useful for raising soil pH and providing nutrients, such as Ca, K, Mg, and P (Chirenje and Ma 2002; Vance 1996). The caveat is that other heavy metals (metalloids) recognized as being pollutants (e.g., Pb, Zn, Cu, Ni, and As) are concentrated in wood due to anthropogenic activities (Odlare and Pell 2009). A significant presence of these metals in the resultant ashes may have major impact on their suitability for application as soil amendments. However, determinations of the total concentrations of these elements are not sufficient to assess the environmental impacts, since their specific chemical forms dictate their mobility, bioavailability, and toxicity (Bruder-Hubscher et al. 2002; Huang et al. 2007; Jamali et al. 2009).

The objectives of the present study were to characterize the basic properties of the carbon-rich fly ash from the processing of wood chips in a commercial gasification-based power generation plant and apply a sequential extraction procedure to assess the leachability/bioavailability elements that would be either beneficial or detrimental to its possible use as a soil amendment. This was compared to inorganic ash generation by combustion (550 °C) of the wood chip feedstock. As a control to assess the impacts of the conditions experienced during gasification (650 to 900 °C), a sample of fly ash was combusted and analyzed in parallel to the wood ash prepared directly from the feedstock. Determining the specific compounds for each element in each of the three ash samples would be impractical. The more reasonable approach used here is the determination of broader defined forms, achieved through the sequential extraction procedures.

## EXPERIMENTAL

### Materials

The fly ash used in this study was collected following the processing of southern yellow pine (mostly *Pinus taeda* L.) pulp grade chips in a commercial 25 kW gasification-based power generation plant (BioMax 25, Community Power Corporation, Littleton, CO). Temperatures within the gasifier ranged from *ca.* 650 °C to *ca.* 900 °C as the feedstock underwent final drying, flaming pyrolysis, char oxidation, and char reduction events leading to the production of synthesis gas and the fly ash byproduct. The producer gas, accompanied by fly ash, passes through a heat exchanger which reduces the temperature of the producer gas from *ca.* 500 °C to about *ca.* 100 °C. The cooled producer gas is then cleaned before use (internal combustion engine, flare) in a filtration system comprised of filter bags. The fly ash was collected in a bin beneath the filter bags and transferred to a separate storage container via an auger. Fly ash, bottom ash, ash clinkers, and debris that accumulated below the gasifier and up to the filtration system, especially in the heat exchanger, were not included in this study. The fly ash in the collection drum, fitted with a heavy plastic liner, was opened with ventilation to allow any combustible and toxic vapors (e.g., CO, H<sub>2</sub>) to dissipate. After about 30 minutes, the drum liner was sealed. All samples were subsequently kept in closed containers and stored in air-conditioned laboratories.

Samples of the carbonaceous fly ash and wood chips were combusted in a laboratory muffle furnace to convert each into inorganic ashes. The fly ash was weighed into porcelain crucibles and heated in the furnace at 550 °C for 6 h to obtain a grey (inorganic) ash. Wood ash was prepared from a sample of the wood chip feedstock by setting the muffle furnace to increasing temperatures and holding it at selected temperatures as follows: 300 °C (1 hr), 400 °C (1 hr), and 550 °C (6 hrs), the final temperature (550 °C) being a routine temperature used for determining the ash content of biomass samples. Reagent grade chemicals were used as received. Purified (Type I) water was used for all experiments.

### Methods

#### *General characterizations of fly ash*

Only the fly ash was tested for moisture, ash, and C, N, and H contents. Values for moisture content, which undoubtedly included volatile organic compounds, were determined by heating samples of the fly ash overnight in an oven (100 °C). Ash (inorganic) contents of the fly ash were determined in a muffle furnace set to 550 °C. The pH of all three ash samples was measured after shaking the samples in purified water for 30 min at room temperature. The solid (fly ash sample) to liquid (purified water) ratio was initially set at 1/10 (Leiva et al. 2007). However, sample issues led us to adjust this ratio to 1/20 (w/w). Combustion analysis was used to determine values for C, N, and H.

#### *Determination of total metal concentration in ash samples by aqua regia digestion*

Samples of (fly) ash (*ca.* 0.500 g) were accurately weighed into glass digestion tubes. Purified water (0.5 g) was used to wet the dusty samples. Then, 12.0 M HCl (6

mL), 15.8 M HNO<sub>3</sub> (2 mL) were added in a dropwise manner to each tube. All tubes were allowed to stand for 16 h at room temperature before refluxing for 2 h at 120 °C. The reflux condenser was then removed and the volume of liquid in each tube was reduced to between 1.5 and 2 mL. The contents of each tube were then rinsed with 0.5 M HNO<sub>3</sub> into a volumetric flask (50 mL). After any solids (presumably undigested silicates) had settled, the liquid was decanted and subjected to elemental analysis by the inductive coupled plasma atomic emission spectroscopy (ICP-AES).

#### *Sequential extraction procedure*

A modified three-step BCR (Bureau Communautaire de Références, now Standards, Measurement and Testing Programme) sequential extraction procedure (Rauret et al. 2000) was used to assess the extractable elements in the three ash samples. The BCR extraction protocol fractionates metal elements in ash samples into four different fractions for each step in the procedure: fraction #1, exchangeable/acid extractable; fraction #2, easily reducible; fraction #3, oxidizable; and fraction #4, residual (Mossop and Davidson et al. 2003). Samples of oven-dried ash samples (0.5 g) were accurately weighed (3 significant figures) into 50 mL polyethylene centrifuge tubes and extracted as follows:

*Step 1.* An aqueous acetic acid solution (0.11 M, 20 mL) was added and the tubes shaken for 16 h at room temperature using an orbital shaker. Fraction #1 was separated from the solid residues by centrifugation (3000 × g, 20 min.) and set aside for subsequent analysis. Purified water (10 mL) was added to the residue which was then shaken for 15 minutes. After centrifugation, the resultant supernatants were discarded and the residue subjected to the second extraction step.

*Step 2.* A freshly prepared hydroxylamine hydrochloride solution (0.5 M, 20 mL) was added to each of the residues, still in the centrifuge tubes from step 1, and shaken for 16 hours. Fraction #2 was separated and the residue rinsed as in step 1.

*Step 3.* Hydrogen peroxide (30%, 5 mL) was added to each of the residues from step 2, still in the centrifuge tubes. The tubes were loosely covered to prevent substantial loss of hydrogen peroxide. Digestion at room temperature was allowed to proceed for 1 h with occasional manual shaking followed by digestion (85 °C, 1 h). The tubes were then uncovered and heating continued to reduce the volume to between 1 and 1.5 mL. Hydrogen peroxide (30%, 5 mL) was again added to each tube. After covering, the samples were further digested (85 °C, 1 h). Volumes were again reduced to between 1 to 1.5 mL. An aqueous solution of ammonium acetate (1.0 M, 25 mL) was then added to each tube. After shaking for 16 h at room temperature, the collection of the supernatant (fraction #3), and rinsing of the residues, was repeated as in step 1.

*Step 4.* Residue from step 3 was transferred to a glass digestion tube and digested with *aqua regia* as described above (fraction #4). This step, which is not part of the original BCR procedure, was for quality control with the sum of step 1-4 being compared with results obtained directly by *aqua regia* digestion (Rauret et al. 2000). All extracting samples from steps 1-4 were analyzed by ICP-AES without further dilution.

## RESULTS AND DISCUSSION

### Yield and General Analyses of Fly Ash

Processing wood chips, at an average rate of 23 kg/hr, gave a black/sooty fly ash with a 0.7% yield of material in the collection drum (Eberhardt et al. 2011). Table 1 presents some general properties of the fly ash used in the present study. Its ash (inorganic) content, determined by ashing at 550 °C, was 50.9% after correcting for a moisture (including light organics) content of 1.9%. Thus, the amount of char was estimated to be about one half of the mass of the sample, which was confirmed by combustion analysis with a carbon content of 47.6%. This result approached the higher end of the range of carbon contents (10 to 60%) for gasifier fly ashes from biomass (Leiva et al. 2007).

**Table 1.** General Chemical Properties of the Fly Ash

---

|                 |       |
|-----------------|-------|
| Ash (inorganic) | 50.9% |
| Carbon          | 47.6% |
| Hydrogen        | 0.82% |
| Nitrogen        | 0.15% |
| pH              | 9.5   |

---

The pH of the fly ash was 9.5, which was slightly lower than that of the wood ash (10.5) prepared from the same feedstock. Treatment of the fly ash in a muffle furnace to remove the residual carbon resulted in a slightly lower pH (9.0). The lower pH for the fly ash, compared to that of the wood ash could be related to the much higher temperatures reached during gasification, resulting in ash melting (Zevenhoven-Onderwater et al. 2001). The high pH for all three ash samples is consistent with the occurrence of basic metal salts, oxides, hydroxides, and/or carbonates (Van Herck and Vandecasteele 2001). However, the high amount of carbon in the fly ash, and associated undesirable organic compounds (e.g., polycyclic aromatic hydrocarbons), may be best removed before field application; various options for co-firing (power plants, incinerators, boilers, and cement kilns) have been suggested, but such pretreatments may be cost/resource prohibitive (Gomez-Barea et al. 2009).

### Total Nutrient Elements and Heavy Metal Contaminants

Total contents of selected nutrient elements (Cu, Mg, K, P, Mn, and B) in the fly ash, the inorganic grey ash derived from it by combustion, and the wood ash, obtained by combustion of the wood chip feedstock, are presented in Table 2. Consistent with the high pH values, there were high concentrations of alkali and alkaline earth metals. The nutrient element concentrations for the fly ash were roughly one half those for the combusted fly ash, which is obviously related to roughly one half of the fly ash being carbon.

**Table 2.** Total Nutrient Element Concentrations in Ash Samples (g kg<sup>-1</sup>)

|                   | Ca               | Mg              | K                | P               | Mn              | B               |
|-------------------|------------------|-----------------|------------------|-----------------|-----------------|-----------------|
| Wood ash          | 130.65<br>(2.12) | 44.13<br>(1.66) | 129.47<br>(0.33) | 11.76<br>(0.41) | 12.32<br>(0.50) | 0.71<br>(0.03)  |
| Combusted fly ash | 134.71<br>(1.33) | 17.06<br>(0.19) | 44.19<br>(0.57)  | 5.35<br>(0.12)  | 8.78<br>(0.25)  | 0.28<br>(0.03)  |
| Fly ash           | 75.57<br>(0.41)  | 7.91<br>(0.02)  | 20.33<br>(0.11)  | 2.44<br>(0.02)  | 4.20<br>(0.03)  | 0.14<br>(<0.01) |

\*Numbers in parentheses are standard deviation, n=3

The compositions of the wood ash and the combusted fly ash were of specific interest for direct comparison, both being inorganic grey ashes. Although ultimately derived from the same biomass feedstock, these two ashes passed through different temperature regimes. The impacts of these different temperature regimes may have contributed to the differences in concentration for each element between these two ash samples. Among the nutrient elements analyzed, calcium was the most stable, with similar levels in the wood ash and the combusted fly ash. The fly ash from gasification has been reported to be dominated by Ca minerals due to the high level of Ca compounds naturally occurring in wood (Van Herck and Vandecasteele 2001). Aside from Ca present as Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, the wood ash likely contained CaCO<sub>3</sub> with the higher temperatures during gasification converting this later form to the oxide (Ljung and Nordin 1997).

Substantial loss of potassium was observed in the combusted fly ash when compared to that of the wood ash; the amount of K in the combusted fly was one third that found in the wood ash. According to Ljung and Nordin (1997), K starts to form gaseous hydroxides between 800 and 850 °C. The temperature reached within the gasifier exceeded this range, and thus we account for the loss of K in the combusted fly ash through this mechanism.

Lower concentrations of Mg and P in the combusted fly ash, which typically form stable solid MgO and phosphates (e.g., Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) up to 1500 °C (Ljung and Nordin 1997), might be suggested to be an inconsistent result. However, given the chemical complexity of the ashes, especially the impacts from other elements such as chlorine and sulfur (Ljung and Nordin 1997), it is difficult to rationalize all differences without being excessively speculative. Nevertheless, it can be stated with reasonable confidence that the conditions experienced during gasification, especially the high temperatures (650 to 900 °C), did have an impact on the proportions of nutrient elements.

As for the total concentration of each nutrient element, both fly ash and combusted fly char ash have higher nutrient element contents than reported values of the typical topsoil collected from the northern part of the US (Mozaffari et al. 2000), thus suggesting their potential application as both a liming agent for acidic soils and a source of macro- and micronutrients.

**Table 3.** Total Heavy Metal Concentrations in Ash Samples (mg kg<sup>-1</sup>)

|                            | Cd              | Cr               | Cu               | Ni              | Pb              | Zn               | As               |
|----------------------------|-----------------|------------------|------------------|-----------------|-----------------|------------------|------------------|
| Wood ash                   | 16.71<br>(0.49) | 8.34<br>(0.83)   | 198.59<br>(0.99) | 20.63<br>(0.52) | 36.27<br>(0.77) | 4387.13<br>(170) | 9.20<br>(3.42)   |
| Combusted fly ash          | 9.57<br>(0.11)  | 60.36<br>(2.99)  | 73.92<br>(2.03)  | 81.22<br>(3.00) | 22.95<br>(1.05) | 777.84<br>(17.2) | 8.89<br>(0.79)   |
| Fly ash                    | 4.39<br>(0.09)  | 38.51<br>(11.50) | 37.25<br>(3.64)  | 47.29<br>(3.27) | 11.83<br>(0.17) | 345.45<br>(5.05) | 10.06<br>(10.90) |
| Eco-SSL value <sup>1</sup> | 32              | 130              | 70               | 38              | 120             | 160              | 18               |

\*Numbers in parentheses are the standard deviations, n=3

<sup>1</sup>Eco-SSL values are cited from reference (EPA 2003).

In addition to the presence of beneficial nutrient elements, the concentrations of heavy metals (metalloids) must be taken into account when ashes are considered for use as soil amendments. Table 3 lists the total concentration of 7 heavy metals present in the three ash samples. Similar to that observed above with the nutrient elements, the heavy metal contents of the fly ash were generally lower than those in the wood ash and combusted fly ash, except for Cr and Ni. The contents of these two heavy metals were even higher in combusted fly ash, whereby Cr and Ni were 7 and 4 times higher, respectively, than those in wood ash. Chromium and Ni have been categorized as non- and semi-volatile elements, respectively, based on their volatilities during gasification (Bunt and Waanders 2009; 2010). Other semi-volatile elements, Cu and Zn (Bunt and Waanders 2009), showed the opposite trend and were lower in the combusted fly ash relative to the wood ash. The higher volatility predicted for Zn under conditions within a gasifier (Bunt and Waanders 2009) is consistent with the seemingly greater losses of Zn that were observed in the fly ash. Further research is needed to better address the apparent concentration and/or losses of heavy metals during gasification. Nevertheless, results shown here demonstrate that the conditions within the gasifier afforded an ash with a different proportion of heavy metals than that obtained by simple combustion in a muffle furnace.

The elements Cd, Pb, and As have been classified as volatile under conditions found in a gasifier (Bunt and Waanders 2008). The contents of these elements in the combusted fly ash were slightly lower or essentially the same as in the wood ash. Cadmium, Pb, and As form gaseous species, such as CdO, PbO, and As<sub>4</sub>O<sub>6</sub>, respectively, at temperatures ranging from 550 to 725 °C (Ljung and Nordin 1997; Bunt and Waanders 2008; 2009); under reducing conditions, Cd is volatile at a temperature as low as 325 °C (Bunt and Waanders 2008). Volatilization of these elements did not appear to differ significantly between the treatments, most likely as a function of their already relatively low concentrations.

Specific regulations for the application of biomass-derived fly ashes to forest and agricultural lands in the United States are not currently available, neither for purposes of amending soils nor disposal. However, the United States Environmental Protection Agency (EPA) does provide some targeted guidelines related to land application of

wastes and environmental contamination monitoring/assessments. For example, the EPA has published a process for deriving a set of ecological soil screening levels (Eco-SSL) which can be used to identify soil contaminants that may be of concern for flora and fauna at hazardous waste sites (EPA 2003). Briefly, these values are based on literature reports that were evaluated by multi-stakeholder panel to ultimately derive soil screening values for identifying levels for concern, not guidelines for cleanup efforts (EPA 2003).

**Table 4.** Nutrient Element Concentrations in Ash Samples for Each Fraction in the BCR Sequential Extraction Procedure

|                          | #1               | #2              | #3              | #4               | Sum    | %Recovery |
|--------------------------|------------------|-----------------|-----------------|------------------|--------|-----------|
| <b>Wood ash</b>          |                  |                 |                 |                  |        |           |
| Ca                       | 1.28<br>(0.09)   | 79.54<br>(3.78) | 99.75<br>(8.09) | <0.005           | 180.57 | 138       |
| Mg                       | 28.86<br>(0.41)  | 20.13<br>(1.19) | 1.67<br>(0.24)  | 0.006<br>(0.002) | 50.66  | 114       |
| K                        | 121.42<br>(0.38) | 5.42<br>(0.52)  | 1.51<br>(0.16)  | 1.37<br>(0.83)   | 129.71 | 100       |
| P                        | 0.06<br>(0.002)  | 0.76<br>(0.08)  | 7.02<br>(0.66)  | 3.03<br>(0.46)   | 10.88  | 92        |
| Mn                       | 0.004<br>(0.001) | 12.05<br>(0.54) | 1.93<br>(0.22)  | <0.005           | 14.05  | 114       |
| B                        | 0.45<br>(0.004)  | 0.18<br>(0.008) | 0.13<br>(0.012) | <0.005           | 0.76   | 107       |
| <b>Combusted fly ash</b> |                  |                 |                 |                  |        |           |
| Ca                       | 61.66<br>(1.58)  | 98.69<br>(3.66) | 12.24<br>(0.88) | <0.005           | 172.59 | 128       |
| Mg                       | 12.4<br>(0.15)   | 3.75<br>(0.16)  | 1.14<br>(0.38)  | 0.007<br>(0.004) | 17.29  | 101       |
| K                        | 12.67<br>(0.12)  | 3.75<br>(0.13)  | 7.61<br>(0.38)  | 17.9<br>(1.42)   | 41.92  | 95        |
| P                        | <0.005           | <0.005          | 2.7<br>(0.09)   | 2.47<br>(0.06)   | 5.20   | 97        |
| Mn                       | 0.008<br>(0.001) | 8.56<br>(0.33)  | 0.65<br>(0.04)  | 0.006<br>(0.001) | 9.22   | 105       |
| B                        | 0.18<br>(0.02)   | 0.06<br>(0.003) | 0.05<br>(0.004) | <0.005           | 0.29   | 104       |
| <b>Fly ash</b>           |                  |                 |                 |                  |        |           |
| Ca                       | 68.97<br>(2.06)  | 19.32<br>(1.0)  | 1.16<br>(0.09)  | 0.01<br>(0.004)  | 89.47  | 118       |
| Mg                       | 6.7<br>(0.34)    | 1.46<br>(0.02)  | 0.17<br>(0.01)  | <0.005           | 8.34   | 105       |
| K                        | 6.7<br>(0.13)    | 5.82<br>(0.06)  | 2.93<br>(0.07)  | 4.11<br>(0.86)   | 19.56  | 96        |
| P                        | 0.005<br>(0.002) | 2.17<br>(0.008) | 0.01<br>(0.003) | 0.01<br>(0.002)  | 2.33   | 95        |
| Mn                       | 3.09<br>(0.19)   | 1.30<br>(0.03)  | 0.10<br>(0.007) | <0.005           | 4.50   | 107       |
| B                        | 0.09<br>(0.005)  | 0.04<br>(0.006) | 0.02<br>(0.006) | <0.005           | 0.15   | 107       |

\*The results are expressed as the mean with standard deviations in parentheses in  $\text{g kg}^{-1}$  of dry matter (n=3)



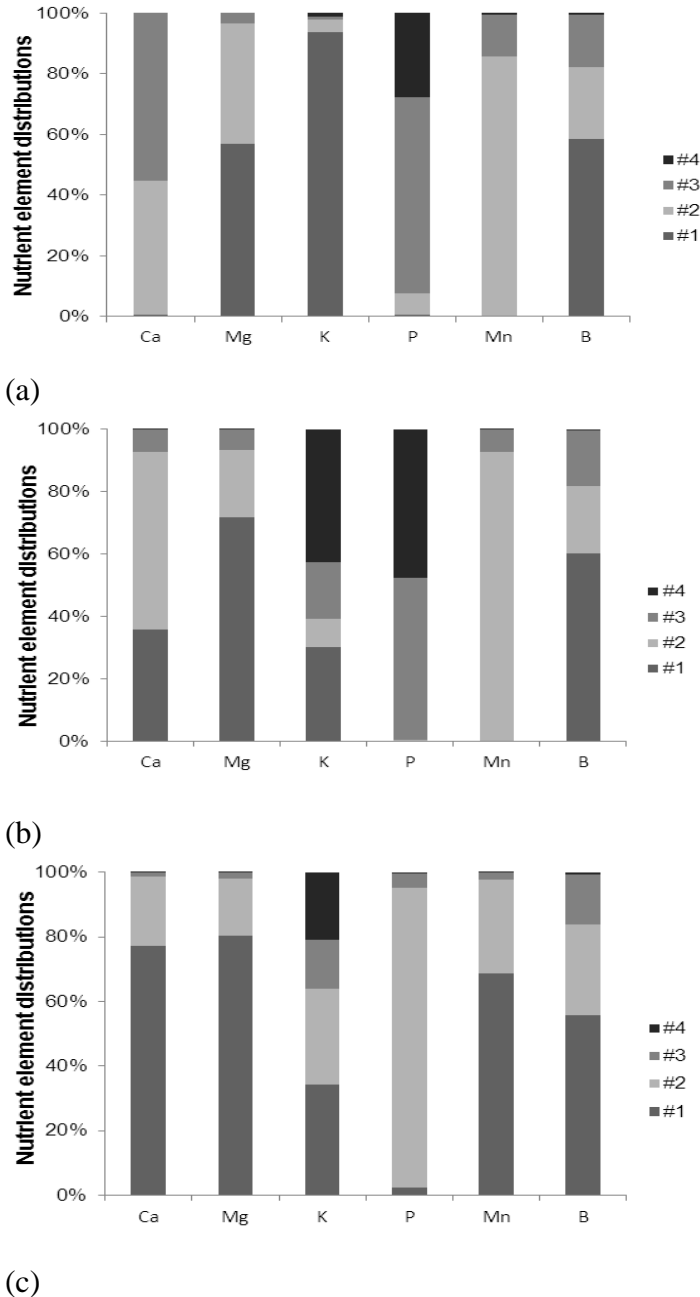
In this study, the concentrations of Cd, Cr, Pb, and As in the fly ash and combusted fly ash were all lower than the reported screening levels. For Cu, the concentration in the fly ash was below the Eco-SSL value but higher after combustion. The concentrations of Ni and Zn in the fly ash, before and after combustion, exceeded the Eco-SSL values. The high concentration of these two metals is undoubtedly related to the wood chip feedstock, because the wood ash from this feedstock also had high levels of Zn and Ni.

Zn and Ni may be phytotoxic, but are not normally hazardous to humans (ICRCL 1987). In European countries, the acceptable threshold levels of Zn and Ni in open space soil are 300 and 70 mg kg<sup>-1</sup>, respectively (ICRCL 1987). Forest soils are normally thinner and often more acidic compared to agricultural soil. Therefore, combustion ashes could be used specifically as a forest soil liming agent or as a fertilizer when elevating the soil pH is not a concern. The limits of Zn and Ni in forest fertilizer recommended by another guideline put forth by the Swedish Forestry Board (2002) are 7.0 and 0.07 g kg<sup>-1</sup>. Thus, the fly ash and combusted fly ash in the present would appear to be nearly suitable for application on forestlands.

### Element Distribution and Bioavailability

Total concentrations of major and trace elements in ash samples may be informative as to the presence of nutrients or potentially hazardous heavy metal contaminants, but provide little indication of their bioavailability, mobility, and other essential properties related to their true environmental and ecological impacts (Ahnstrom and Parker 1999). Sequential extraction analysis of major and trace metals in soil or other solid waste is a practical technique to determine broader defined forms, e.g. so-called “mobile” or “carbonate bound” forms of the major and trace metals in such solid samples (Basta et al. 2005). Although chemical methods differ from living plants in their abilities to extract plant nutrients from soil, good correlations between chemical extractions and plant uptake data has allowed the use of such extractions to make reasonable predictions of plant-available nutrients and the possible uptake of pollutant heavy metals by plants (Basta et al. 2005).

The BCR extraction protocol fractionates metal elements in ash samples into four different fractions for each step in the procedure: fraction #1, exchangeable/acid extractable; fraction #2, easily reducible; fraction #3, oxidizable; and fraction #4, residual (Mossop and Davidson et al. 2003). It is generally defined the ‘bioavailable/mobile pool’ as the most easily extracted fractions (corresponding to the fraction #1 of the BCR procedure). However, studies may also define fractions #2 and #3 as having a certain degree of bioavailability. Fraction #4 is always considered not being bioavailable (Bacon and Davidson 2008). Here, we define fraction #1 as bioavailable and fractions #2 and #3 and potentially bioavailable, to provide some level of gradation. Table 4 and Fig. 1 demonstrate the distributions of the selected nutrient elements by BCR extraction in the three different ash samples. The percent recovery of all elements from the BCR procedures ranged from 92 to 138%; reported recoveries in excess of 100% are typical (Mossop and Davidson 2003, Rauret et al 1999, Tokalioglu et al. 2003) and reflect the limits of comparing the sum of the values for all fractions with values determined by digestion of the whole sample in reagents such as *aqua regia*.



**Fig. 1.** Normalized nutrient element distribution patterns for each fraction in the BCR sequential extraction procedure: (a) wood ash, (b) combusted fly ash, and (c) fly ash

Figure 1 shows that most elements had different distribution patterns between the three different ash samples used in this study. The amounts of Ca in the exchangeable/acid extractable fraction (#1) were in the following order: fly ash > combusted fly ash > wood ash. It appears that the conditions in the gasifier promoted the formation of readily soluble calcium species. This fraction is considered to be the most readily available for plant uptake (Kazi et al. 2005). Metals in the easily reducible

fraction (#2) can be mobilized with reducing conditions in the environment, and thus are also potentially bioavailable (Nurmesniemi et al. 2008). Accordingly, over 90% of Ca in fly ash and combusted fly ash were present in these two fractions and would be potentially bioavailable.

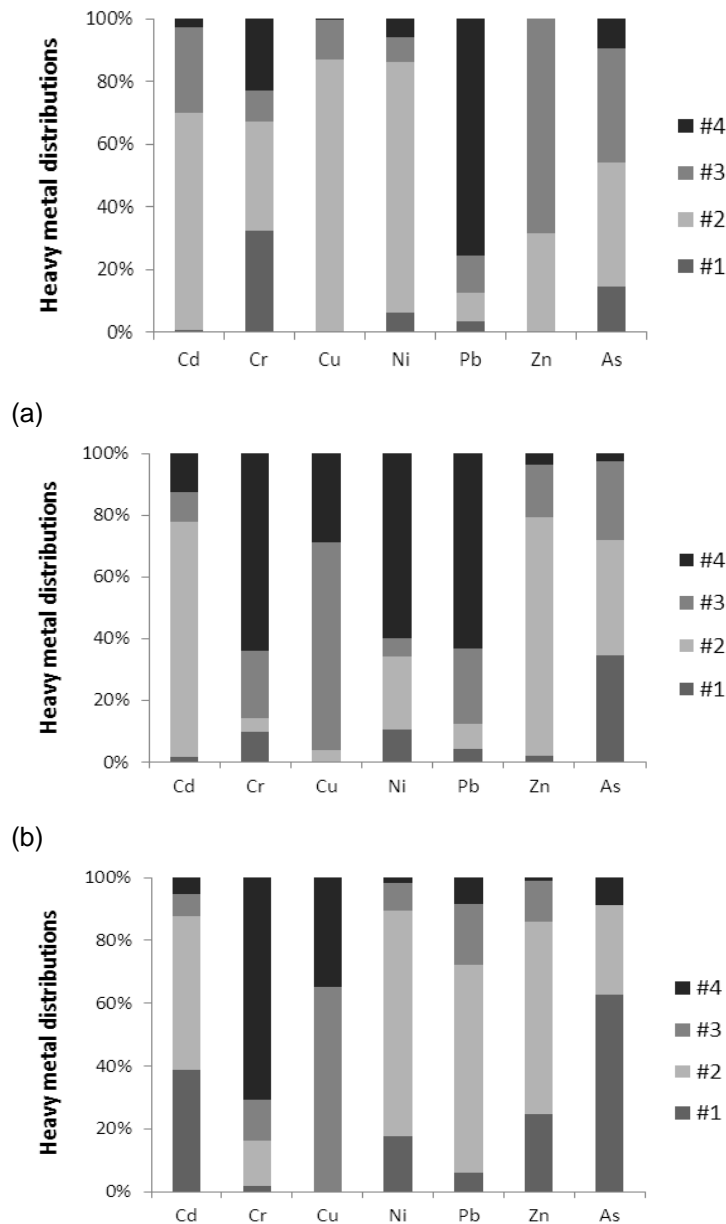
In an analogous manner, the other nutrient elements show some partitioning between the different fractions. For example, the majority of Mg was present in exchangeable/acid extractable (#1) and easily reducible (#2) fractions in all three types of ash; however, unlike that for Ca, the proportions in exchangeable/acid extractable (#1) and reducible (#2) fractions were in an opposite order: fly ash < combusted fly ash < wood ash. Whereas Ca was more exchangeable/acid extractable in the fly ash, Mg was more exchangeable/acid extractable in the wood ash. For K, the relative amounts in the reducible (#2) and residue (#4) fractions were higher for fly ash and combusted fly ash samples. In the wood ash, K was predominantly in the exchangeable/acid extractable fraction (#1). Accordingly, the conditions of gasification had a significant impact on the bioavailability of this important plant nutrient. In the case of Mn, a similar distribution pattern was observed for the two inorganic ashes, with most of this element being in the reducible (#2) fraction. Since Mn in the fly ash before combustion was present predominately in the exchangeable/acid extractable (#1) fraction, combustion reduced the bioavailability of this element. Boron was the only selected macronutrient element that displayed similar distribution patterns in all three ash samples. Among the nutrient elements, phosphorus appeared to be the least bioavailable in all three ash samples used in this study. More than 90% of P was present in oxidizable (#3) and residual (#4) fractions in wood ash and combusted fly ash. Phosphorus in the fly ash was more accessible than that in the other two ashes, and about 93% was found in the reducible fraction (#2). Other studies on waste incinerator fly ashes reported that metals tended to be concentrated in the exchangeable and carbonate bound (i.e., acid extractable) fractions (Huang et al. 2007; Xue et al. 2010). The results from the BCR extraction analysis suggested that the bioavailability of the nutrient elements may be dependent upon the thermal history of each sample. Therefore, even the analysis of the fly ash cannot simply be extended to represent the bioavailability of the nutrient elements in the combusted fly ash. Dissimilarity in the results for all three samples demonstrate that the analysis of the feedstock is a poor predictor for the suitability of fly ashes for utilization as a soil amendment and the impact on nutrient bioavailability and subsequent treatments (e.g., simple combustion) cannot be discounted.

The distributions of selected heavy metals are shown in Table 5 and Fig. 2. Warranting specific attention are Cu, Ni, and Zn because the amounts of these three heavy metals in the ash samples were close to or exceeded the threshold levels in the Eco-SSL. Copper was in relatively stable forms in both fly ash and combusted fly ash but not the wood ash. It was present predominately in the oxidizable (#3) fraction (65% in fly ash and 67% in combusted fly ash) and the residual (#4) fraction (35% in fly ash and 29% in combusted fly ash). In the oxidizable fraction (#3), metals are organically bound or occur as oxidizable minerals, such as sulfide (Nurmesniemi et al. 2008). Metals in the residual fraction are normally considered non-mobile, retained within the crystal lattice of minerals and inside crystallized oxides. Copper in these fractions would not be

**Table 5.** Heavy Metal Concentrations in Ash Samples for Each Fraction in the BCR Sequential Extraction Procedure

|                          | #1               | #2                | #3               | #4              | Sum    | %Recovery |
|--------------------------|------------------|-------------------|------------------|-----------------|--------|-----------|
| <b>Wood ash</b>          |                  |                   |                  |                 |        |           |
| Cd                       | 0.13<br>(0.10)   | 12.35<br>(0.44)   | 4.86<br>(0.48)   | 0.51<br>(0.06)  | 17.85  | 107       |
| Cr                       | 2.88<br>(0.24)   | 3.08<br>(0.16)    | 0.87<br>(0.08)   | 2.04<br>(0.35)  | 8.87   | 106       |
| Cu                       | 0.68<br>(0.39)   | 192.05<br>(9.19)  | 28.87<br>(1.82)  | 0.43<br>(0.04)  | 222.02 | 112       |
| Ni                       | 1.65<br>(0.17)   | 20.60<br>(0.47)   | 2.06<br>(0.34)   | 1.47<br>(0.38)  | 25.78  | 125       |
| Pb                       | 1.18<br>(0.45)   | 2.92<br>(0.23)    | 3.86<br>(0.83)   | 24.58<br>(1.56) | 32.49  | 90        |
| Zn                       | 17.64<br>(4.05)  | 1537<br>(143)     | 3353<br>(340)    | 5.6<br>(0.09)   | 4912.6 | 112       |
| As                       | 2.06<br>(1.42)   | 5.52<br>(4.84)    | 5.07<br>(2.79)   | 1.32<br>(0.06)  | 13.97  | 152       |
| <b>Combusted fly ash</b> |                  |                   |                  |                 |        |           |
| Cd                       | 0.14<br>(0.17)   | 6.24<br>(0.24)    | 0.79<br>(0.05)   | 1.03<br>(0.03)  | 8.19   | 86        |
| Cr                       | 6.06<br>(0.55)   | 2.83<br>(0.04)    | 13.64<br>(1.04)  | 39.6<br>(2.05)  | 62.13  | 103       |
| Cu                       | 0.20<br>(0.11)   | 2.55<br>(0.19)    | 47.72<br>(2.59)  | 20.3<br>(0.87)  | 70.77  | 96        |
| Ni                       | 10.06<br>(0.43)  | 22.21<br>(0.99)   | 5.68<br>(1.31)   | 56.34<br>(1.79) | 94.26  | 116       |
| Pb                       | 1.10<br>(0.29)   | 2.01<br>(0.04)    | 6.21<br>(0.48)   | 15.93<br>(0.89) | 25.23  | 110       |
| Zn                       | 17.11<br>(9.79)  | 602.42<br>(23.15) | 131.01<br>(9.95) | 29.73<br>(1.27) | 780.23 | 100       |
| As                       | 4.63<br>(3.45)   | 5.01<br>(4.53)    | 3.39<br>(1.96)   | 0.34<br>(0.08)  | 13.37  | 150       |
| <b>Fly ash</b>           |                  |                   |                  |                 |        |           |
| Cd                       | 1.88<br>(0.17)   | 2.36<br>(0.16)    | 0.34<br>(0.06)   | 0.25<br>(0.06)  | 4.84   | 110       |
| Cr                       | 0.80<br>(0.09)   | 5.82<br>(0.29)    | 5.31<br>(0.55)   | 28.6<br>(0.42)  | 40.53  | 105       |
| Cu                       | 0                | 0                 | 25.58<br>(1.49)  | 13.75<br>(0.12) | 39.28  | 105       |
| Ni                       | 8.34<br>(1.06)   | 34.28<br>(1.94)   | 4.24<br>(0.15)   | 0.79<br>(0.04)  | 47.65  | 101       |
| Pb                       | 0.98<br>(0.56)   | 10.49<br>(0.85)   | 3.04<br>(0.15)   | 1.33<br>(0.08)  | 15.84  | 134       |
| Zn                       | 100.85<br>(1.16) | 249.71<br>(13.5)  | 52.82<br>(1.99)  | 4.56<br>(0.79)  | 407.94 | 118       |
| As                       | 6.01<br>(1.16)   | 2.74<br>(1.69)    | 0                | 0.85<br>(0.13)  | 9.60   | 95        |

\*The results are expressed as the mean with standard deviations in parentheses in mg kg<sup>-1</sup> of dry matter (n= 3)



(C)

**Fig. 2.** Normalized heavy metal distribution patterns for each fraction in the BCR sequential extraction procedure: (a) wood ash, (b) combusted fly ash, and (c) fly ash

dissolved under the conditions normally found in nature (Tessier et al. 1979). In general terms, Ni and Zn were present in less mobile fractions in combusted fly ash than in fly ash. More than one half of the recovered Ni was found in the residue fraction (#4) of the combusted fly ash, whereas in the other two samples relatively little Ni was found in this fraction. The interesting observation for Zn was that the relative proportion in the exchangeable/acid fraction (#1) for the fly ash was reduced significantly upon the simple operation of combustion. Again, this demonstrated that thermal treatments of the fly ash

have a significant impact on the bioavailability of elements, in this case, potentially hazardous contaminants.

Of the other heavy metals (metalloids) that were below the Eco SSLs, Cd and As were the most mobile. Chromium was present in a high percentage in oxidizable (#3) and residual (#4) fractions for the fly ash before and after combustion. It is interesting to note that the stability of Pb in the fly ash was increased by combustion. No all-encompassing trends were observed in the distributions of the heavy metals among three types of ash samples used in this study. Some elements, such as Cr and Cu, tended to form more stable species when exposed to the high temperatures of gasification. Others acted in the opposite way, such as Cd and As. At this juncture it should be noted that the fate of heavy metals during the gasification of the feedstock, or subsequent combustion of the resultant fly ash, could be impacted by many factors other than just temperature. Determining the exact chemical species of these heavy metals is beyond the scope of the BCR sequential extraction procedure. However, the results from this analysis have shown that high proportion of the heavy metals present in these sample are of limited mobility. Samples with total concentrations of heavy metals below any threshold values, such as those used herein, should present limited concern if used as forest fertilizers.

## CONCLUSIONS

1. Processing conditions played an important role in determining the total metal concentrations in three different types of ash samples. The concentration of those elements that have high boiling points or could form stable species at high temperature (e.g., Ca, Cr, and Ni), were maintained at similar levels in wood ash and combusted fly ash. On the other hand, substantial losses were observed for those metals with low boiling points in combusted fly ash when compared to that of wood ash (e.g., K, Cd, Pb, Zn, and As).
2. The amount of unburned carbon in the fly ash can be used to account for the increase in concentration of each element in the combusted fly ash.
3. The concentrations of most heavy metals in ash samples in this study were lower than the Eco-SSLs set by the EPA except for Ni and Zn. However, the concentrations of Ni and Zn were still within the acceptable levels for use of the fly ash as a forest fertilizer using standards for the application of wood ashes on forestlands.
4. The distribution patterns of most metals in three types of ash samples were different for the fractions collected by the BCR sequential extraction procedure. Nutrient elements were generally more bioavailable in fly ash than in combusted fly ash. Except for K, the elements in the fly ash had a higher bioavailability than that of the elements in the wood ash.
5. The heavy metals were not completely bioavailable in the fly ash or combusted fly ash. Therefore, the environmental impact during land application of fly ash may be significantly lower than that suggested on the basis of the total heavy metal concentrations from standard digestions and elemental analyses.

## ACKNOWLEDGMENTS

Brandi Downs (Louisiana State University Agricultural Center) carried out the digestions for ICP-AES. Karen Reed (USDA Forest Service) assisted with the ash and volatile matter determinations. ICP-AES was conducted by Dr. Robert P. Gambrell (Louisiana State University Wetland Biogeochemistry Analytical Services). Drs. Les Groom, Tom Elder, and Chi-Leung So (USDA Forest Service) kindly helped in collecting the fly ash samples.

## REFERENCES CITED

- Ahnstrom, Z. S., and Parker, D. R. (1999). "Development and assessment of a sequential extraction procedure for the fractionation of soil cadmium," *Soil Sci. Soc. Am. J.* 63, 1650-1658.
- Bacon, J. R., and Davidson, C. M. (2008). "Is there a future for sequential chemical extraction?" *Analyst* 133, 25-46.
- Basta, N. T., Ryan, J. A., and Chaney, R. L. (2005). "Trace element chemistry in residual-treated soil: key concepts and metal bioavailability," *J. Environ. Qual.* 34, 49-63.
- Brewer, C. E., Schmidt-Rohr, K., Satrio, J. A., and Brown, R. C. (2009). "Characterization of biochar from fast pyrolysis and gasification systems," *Environmental Progress & Sustainable Energy* 28(3), 386-396.
- Bruder-Hubscher, V., Lagarde, F., Leroy, M. J. F., Coughanowr, C., and Enguehard, F. (2002). "Application of a sequential extraction procedure to study the release of elements from municipal solid waste incineration bottom ash," *Analytica Chimica Acta* 451, 285-295.
- Bunt, J. R., and Waanders, F. B. (2008). "Trace element behavior in the sasol-Lurgi MK IV FBDB gasifier. Part 1 - The volatile elements: Hg, As, Se, Cd and Pb," *Fuel* 87, 2374-2387.
- Bunt, J. R., and Waanders, F. B. (2009). "Trace element behavior in the sasol-Lurgi MK IV FBDB gasifier. Part 2 - The semi-volatile elements: Cu, Mo, Ni, and Zn," *Fuel* 88, 961-969.
- Bunt, J. R., and Waanders, F. B. (2010). "Trace element behavior in the sasol-Lurgi fixed-bed dry-bottom gasifier. Part 3 - The non-volatile elements: Ba, Co, Cr, Mn, and V," *Fuel* 89, 537-548.
- Chan, K. Y., Zwieten, L. V., Meszaros, I., Downie, A., and Joseph, S. (2008). "Using poultry litter biochars as soil amendments," *Aust. J. Soil Res.* 46, 437-444.
- Chirenje, T., and Ma, L. Q. (2002). "Impact of high-volume wood-fired boiler ash amendment on soil properties and nutrients," *Commun. Soil Sci. Plant Anal.* 33(1&2), 1-17.
- De Bari, I., Barisano, D., Cardinale, M., Matera, D., Nanna, F., and Viggiano, D. (2000). "Air gasification of biomass in a downdraft fixed bed: a comparative study of the inorganic and organic products distribution," *Energy Fuels* 14, 889-898.

- Eberhardt, T. L., Pan, H., Groom, L. H., and So, C.-L. (2011). "Characterization and partitioning of the char ash collected after the processing of pine wood chips in a pilot-scale gasification plant," *In Proceedings of the International Conference on Woody Biomass Utilization*, Starkville, MS, August 4-5, 2009. Edited by J. R. Shelly (Madison, WI. Forest Products Society), pp. 33-38.
- Gomez-Barea, A., Vilches, L. F., Leiva, C., Campoy, M., and Fernandez-Pereira, C. (2009). "Plant optimization and ash recycling in fluidized bed waste gasification," *Chem. Eng. J.* 146, 227-236.
- Huang, S. J., Chang, C. Y., Mui, D. T., Chang, F. C., Lee, M. Y., and Wang, W. F. (2007). "Sequential extraction for evaluating the leaching behavior of selected elements in the municipal solid waste incineration fly ash," *J. Hazard Mater.* 149, 180-188.
- Interdepartmental Committee on the redevelopment of Contaminated Land (ICRCL) (1987). "Guidance on the assessment and redevelopment of contaminated land," Guidance Note 59/83. Department of the Environment, London.
- Jamali, M. K., Kazi, T. G., Arain, M. B., Afridi, H. I., Jalbani, N., Kandhro, G. A., Shah, A. Q., and Baig, J. A. (2009). "Speciation of heavy metals in untreated sewage sludge by using microwave assisted sequential extraction procedure," *J. Hazardous Mat.* 163, 1157-1164.
- Kazi, T. G., Jamali, M. K., Kazi, G. H., Arain, M. B., Afridi, H. I., Siddiqui, A. (2005). "Evaluating the mobility of toxic metals in untreated industrial wastewater sludge using a BCR sequential extraction procedure and a leaching test," *Anal. Bioanal. Chem.* 383, 297-304.
- Kramreiter, R., Url, M., Kotik, J., and Hofbauer, H. (2008). "Experimental investigation of a 125 kW twin-fire fixed bed gasification pilot plant and comparison to the results of a 2 MW combined heat and power plant," *Fuel Processing Tech.* 89, 90-102.
- Kumar, A., Jones, D. D., and Hanna, M. A. (2009). "Thermochemical biomass gasification: A review of the current status of the technology," *Energies* 2, 556-581.
- Leiva, C., Gomez-Barea, A., Vilches, L. F., Ollero, P., Vale, J., and Fernandez-Pereira, C. (2007). "Use of biomass gasification fly ash in lightweight plasterboard," *Energ. Fuel* 21, 361-367.
- Liao, C., Wu, C, and Yan, Y. (2007). "The characteristics of inorganic elements in ashes from a 1 MW CFP biomass gasification power generation plant," *Fuel Processing Tech.* 88, 149-156.
- Ljung, A., and Nordin, A. (1997). "Theoretical feasibility for ecological biomass ash recirculation: chemical equilibrium behavior of nutrient elements and heavy metals during combustion," *Environ. Sci. Technol.* 31, 2499-2503.
- Mossop, K. F., and Davidson, C. M. (2003), "Comparison of the original and modified BCR extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments," *Analytica Chimica Acta* 478, 111-118.
- Mozaffari, M., Rosen, C. J., Russelle, M. P., and Nater, E. A. (2000). "Chemical characterization of ash from gasification of alfalfa stems: Implications for ash management," *J. Environ. Qual.* 29, 963-972.



- Mozaffari, M., Russelle, M. P., Rosen, C. J., and Nater, E. A. (2002). "Nutrient supply and neutralizing value of alfalfa stem gasification ash," *Soil Sci. Soc. Am. J.* 66, 171-178.
- Nurmesniemi, H. Poykio, R., Kuokkanen, T., and Ramo, J. (2008). "Chemical sequential extraction of heavy metals and sulphur in bottom ash and fly ash from a pulp and paper mill complex," *Waste Manag. Res.* 26, 389-399.
- Odlare, M., and Pell, M. (2009). "Effect of wood fly ash and compost on nitrification and denitrification in agricultural soil," *Appl. Energy* 86, 74-80.
- Pitman, R. M. (2006). "Wood ash use in forestry-a review of the environmental impacts," *Forestry* 79(5), 563-588.
- Rauret, G., López-Sánchez, J. F., Sahuquillo, A., Davidson, C., Ure, A., and Quevauviller, Ph. (1999). "Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials," *J. Environ. Monitor.* 1, 57-61.
- Rauret, G., López-Sánchez, J. F., Sahuquillo, A., Barahona, E., Lachica, M., Ure, A.M., Davidson, C.M., Gomez, A., Lück, D., Bacon, J., Yli-Halla, M., Muntau, H., and Quevauviller, Ph. (2000). "Application of a modified BCR sequential extraction (three-step) procedure for the determination of extractable trace metal contents in a sewage sludge amended soil reference material (CRM 483), complemented by a three-year stability study of acetic acid and EDTA extractable metal content," *J. Environ. Monitor.* 2, 228-233.
- Swedish National Board of Forestry (2002). "Recommendations for the extraction of forest fuel and compensation fertilizing," Samuelsson, H. (ed.). Skogsstyrelsen (Swedish Forest Agency), Printed by JV, Jönköping, Sweden, 20 pp.
- Tessier, A., Campbell, P. G. C., and Bisson, M. (1979). "Sequential extraction procedure for the speciation of particulate trace metals," *Anal. Chem.* 51(7), 844-851.
- Tokalioglu, S., Kartal, S., and Birol, G. (2003). "Application of a three-stage sequential extraction procedure for the determination of extractable metal contents in highway soils," *Turk. J. Chem.* 27, 333-346.
- Unruh, D., Pabst, K., and Schaub, G. (2010). "Fisher-Tropsch synfuels from biomass: Maximizing carbon efficiency and hydrocarbon yield," *Energy Fuels* 24, 2634-2641.
- United States Environmental Protection Agency (EPA) (2003). Ecological soil screening level guidance and documents, Environmental Protection Agency (<http://www.epa.gov/ecotox/ecossl/>).
- Van Herck, P. V., and Vandecasteele, C. (2001). "Evaluation of the use of a sequential extraction procedure for the characterization and treatment of metal containing solid waste," *Waste Manage.* 21, 685-694.
- Vance, E. D. (1996). "Land application of wood-fired and combination boiler ashes: An overview," *J. Environ. Qual.* 25, 937-944.
- Vervaeke, P., Tack, F. M. G., Navez, F., Martin, J., Verloo, M. G., and Lust, N. (2006). "Fate of heavy metals during fixed bed downdraft gasification of willow wood harvested from contaminated sites," *Biomass Bioenergy* 30, 58-65.
- Xue, J., Wang, W., Wang, Q., Liu, S., Yang, J., and Wui, T. (2010). "Removal of heavy metals from municipal solid waste incineration fly ash by traditional and microwave acid extraction," *J. Chem. Technol. Biotechnol.* 85, 1268-1277.

Yang, F., and Hlavacek, V. (1999). "Recycling of carbon-enriched coal fly ash," *Powder Technology* 104, 190-195.

Zevenhoven-Onderwater, M., Backman, R., Skrifvars, B.-J., and Hupa, M. (2001). "The ash chemistry in fluidized bed gasification of biomass fuels. Part I: predicting the chemistry of melting ashes and ash-bed material interaction," *Fuel* 80, 1489-1502.

Article submitted: May 19, 2011; Peer review completed: August 7, 2011; Revised version received and accepted: August 18, 2011; Published: August 20, 2011.