CHARACTERISATION OF WOOD COMBUSTION FLY ASH IN A CONTEXT OF APPLICABILITY IN AGRICULTURE

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ABSTRACT

Energy policy of the European Union aims to move towards the sustainable and green energetics, therefore, identification and exploitation of renewable energy resources is of high importance in all EU member states. One of the types of renewable energy production is cogeneration of heat and power from biomass. Cogeneration becomes more and more topical in the Baltic States as various kinds of biomass, e.g., forestry and agriculture residues, cultivated plants for biomass are rather easy obtainable. For example, in 2015, in Lithuania more than a half (56%) of energy (power and heat) was produced at cogeneration plants. However, increased energy production from biomass, e.g., wood combustion has led to extended amount of combustion residues – ash. Thus, it requires development of environmentally friendly and cost-effective solutions for possible ash utilization, avoiding ash dumping.

The aim of the study was to investigate fly ash samples generated from wood combustion in two cogeneration plants located in Latvia and Lithuania. Characterization of fly ash involved detection of pH, conductivity, loss-on-ignition, total element content and element composition of fractions. After the 3-step speciation analysis of fly ash samples, water soluble, bioavailable and residual fraction were derived. Concentration of elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Sr, Ti, Tl, V and Zn) was measured using ICP-OES.

Results revealed that fly ash composition depends on type, quality and purity of biomass (wood). High average total amount of Ca (92 g/kg), K (38 g/kg) Mg (12 g/kg), Mn (10 g/kg), P (6 g/kg), Al (3 g/kg), Fe and Na (2 g/kg each) was detected in all ash samples. Most of elements (Al, Ba, Cd, Cu, Co, Mg, Mn, P, Pb, Se, Ti, Tl) more than 90% and Zn, Sr, V more than 80% from the total amount were bound in residual fraction indicating their low bioavailability from fly ash. Only Cr, K, Mo and Ni were found in water soluble or bioavailable fractions in considerable amount (>60%).

Overall assumption is that the wood fly ash can be used in forestry and agriculture in direct applications primary as a source of K and some other micro- and macroelements.

The study was done within the project No.1.1.1.2/VIAA/1/16/029 (*Formula of peat-free soil conditioner with controlled-release fertilizing effect applicable for soil remediation and quality improvement of agricultural production*) and in collaboration between the

Laboratory of Environmental Quality Monitoring (University of Latvia) and the Baltic Institute for Regional Development Ltd.

Keywords: cogeneration residues, wood fly ash, macroelements, microelements

INTRODUCTION

The energy policy of the European Union (EU) aims to move towards the sustainable and green energy, therefore, identification and exploitation of renewable energy resources is of high importance in all the EU member states [1] as well as many other countries with a strong sector of agricultural production.

One of the types of renewable energy production is cogeneration of heat and power from biomass. Cogeneration becomes more and more topical worldwide and in the Baltic States due to the possibility to utilize various kinds of rather easy obtainable biomass, e.g., forestry and agriculture residues or plants cultivated for biomass. For example, in 2015, in Lithuania more than a half (56%) of energy (power and heat) was produced at cogeneration plants [2]. Widely used biomass in the Baltic States for energy production in cogeneration is wood and/or wood residues and/or forestry by-products, as these materials are cheap in price and abundant in quantity. However, in stoves that are using wood or wood pellets as a combustible, a problem appears due to the production of ash in large amounts [3]. The amount of produced ash is impressive, for example, 600,000 tons of peat-wood ash as a by-product is generated just in Finland every year [4].

Environmentally friendly and cost-effective solutions for ash utilization are required, avoiding ash landfilling. Application to agricultural or forest soils has been studied as one of the more feasible options for utilizing biomass-derived combustion ash [5]. Wood ash with its high content of inorganic compounds can be useful for increase of soil pH and provision of nutrients such as Ca, K, Mg and P [6; 7]. If compared to agricultural soils, forest soils usually are thinner and often more acidic. Therefore, combustion ash could be especially useful as a forest soil liming agent or as a fertilizer when elevating the soil pH is not a concern [5].

The most important limiting factor for wide application of combustion ash is presence of metallic elements and metalloids (especially, heavy metals), e.g., Pb, Zn, Cu, Ni, As and organic pollutants in its content [8]. Despite the low concentration and the differences in mobility, heavy metals such as Cd, Cr, Cu, Mn, Ni, Pb, Zn may induce changes in the composition of soil, vegetation and consequently ground and surface waters [9]. However, chemical speciation that significantly affects mobility, bioavailability and toxicity of possibly hazardous metallic elements and metalloids is related to the possible environmental impacts. Thus, only ash derived from the combustion of natural biomass can be applied as a soil fertilizing and improving matter, but ash derived from the combustion of wood waste or chemically treated wood are not appropriate for use as soil improvers due to the high concentration of heavy metals [3; 10; 11].

Due to the characteristic high pH, wood ash application to soils can lead to increase in soil pH [12]. By lowering the soil pH, the mobilization of heavy metals will increase, which is a potential threat for the environment, but application of wood ash will lead to opposite effect on soil because mobility of metallic elements in great extent will be reduced. Nevertheless, application of non-stabilised highly soluble ash may cause such adverse effect as a dramatic increase in soil pH and salt concentration [6].

The aim of the current study was to characterize wood fly ash generated from wood biomass combustion in cogeneration power plant in a context of applicability in agriculture particularly in respect to element content.

MATERIALS AND METHODS

Sampling of wood fly ash. Samples of wood fly ash were obtained in September, 2016, from two cogeneration plants located in Latvia and Lithuania. Seven samples (each 500 g) of wood fly ash were collected during one week. Collection of samples was done by the employees of the cogeneration plant based on developed procedure [11]. Technical specification of the cogeneration power plants involved generation of power/heat (23.8 MW) with a technology of combustion as a moving grate, using fire-tube boiler and applying combustion temperature 950°C with capacity of the equipment 8,000 h per year. The main wood species used were conifers (95%) with a negligible addition of deciduous (5%), namely, birch 3% and alder 2%.

Characterization of wood fly ash. Complete characterization of wood fly ash was performed; however, this paper reveals data only on pH, conductivity, loss-on-ignition, total element content and element composition by fractions.

Measurements of pH and conductivity. 3 g of air-dried grounded ash sample were dissolved in 100 mL deionised water (<0.1 µS/cm, 18 MΩ/cm, Millipore Elix-3). pH_{H2O} was measured using microprocessor pH-meter (pH 213, Hanna Instruments); conductivity was detected using microprocessor conductivity meter (HI9932, Hanna Instruments).

Loss-on-ignition (LOI). LOI included analysis of dry matter, gravimetric water, volatile matter, ash and fixed carbon content of wood fly ash using oven (Plus II Oven, Labassco) for drying of samples at 105°C or muffle furnace (t_{max} = 1100°C, Omron) for burning of samples at 950°C and 750°C.

Element speciation analysis and total element content. After the 3-step element speciation analysis of wood fly ash samples applying modified method [10; 13] following fractions were derived: 1) Fraction of water soluble compounds (by dissolving ash in heated-up deionised water); 2) Fraction of weak acid soluble compounds (by dissolving the rest of sediments from the 1^{st} step in CH_3COOH); 3) Fraction of residues (by dissolving the rest of sediments from the 2^{nd} step in *Aqua regia*). Concentration of elements (Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Sr, Ti, Tl, V and Zn) was measured using ICP-OES (iCAP 7000, Thermo Scientific). Total element content was counted as a sum of concentrations detected at the steps of speciation analysis.

RESULTS AND DISCUSSION

Parameters of potentiometric analysis and LOI. pH values, electrical conductivity, and results of LOI of fly ash are shown in Table 1.

Table 1. Potentiometric and LOI parameters detected for wood fly ash.

Parameter	Detected average value
pH_{H2O}	12.3
Electrical conductivity, mS/cm	13.6
Gravimetric water content, %	1.51
Dry matter content, %	98.49
Volatile matter content, %	8.82
Ash content, %	62.14
Fixed carbon, %	27.53

Results indicated high pH value as it was expected as high pH for ash samples is consistent with the occurrence of basic metal salts, oxides, hydroxides and carbonates [5]. Lower pH values have been reported in other studies of biomass ash, i.e., about pH 9.0-9.8, than detected in the current study; that can be related to specific conditions of combustion process [5; 10]. Other studies also confirm similar ash content, e.g., 50.9% of ash in fly ash samples [5]. Many studies have shown an increase of pH in soil as a result of addition of the wood ash following dissolution of oxides, hydroxides and carbonates from the ash [6; 7]. On the one hand, significant increase in soil pH and electric conductivity in soil is undesirable and may adversely impact plant growth as well as can encourage mineral weathering. On the other hand, alkaline character of wood fly ash can promote acid neutralizing potential in soil and can lead to lower mobility and bioavailability of hazardous elements and reduced acidic leaching of them from soil to water, as well as plant toxicity of such microelements as Al, Mn and Fe can be decreased due to reduced exchangeable amounts of these elements. However, it should be taken into account that ash itself may contain considerable amounts of leaching-able elements. Additionally, fly ash deposition in a sustainable manner can improve soil texture, water holding capacity and aeration, as well as can provide better environmental conditions for some soil microorganisms [14].

Element speciation analysis and total element content. Ash composition depends on fuel used for a combustion, furnace temperature and type. Nutrient content and element composition in ash as well is highly dependent on the source, quality and purity of wood and type of combustion equipment [15]. The results of analyses revealed high average total amount of Ca (92 g/kg), K (38 g/kg) Mg (12 g/kg), Mn (10 g/kg), P (6 g/kg), Al (3 g/kg), Fe and Na (each <2 g/kg) in ash samples (Fig. 1).

Total content of P (6 g/kg) in the tested wood fly ash cannot be assessed as high, nor low, if compared to other studies where P concentration ranged from 10 mg/kg to 14 g/kg. With high pH values also high content of alkali and alkaline metals in wood fly ash was detected. Concentration of K (38 g/kg) is very comparable to the literature data (30-54 g/kg) [7; 15]. P and K dissolution rate and availability are also dependent on soil pH. For consideration of an N, P, K type fertilizer, P and K quantity relations need to be more or less appropriate and also N needs to be added.

Detected elevated content of Na is unfavourable for cultivated plants, and values exceeding 1.6 g/kg can lead to unfavourable salinization; however, if taking into account distribution of Na by fractions, more than 50% of Na is bound in residual fraction which is characterized by its low solubility.

Dominance of Ca in wood fly ash, as it was detected also in the current study, has been reported in the literature as Ca compounds are naturally occurring in wood in high concentration [5].

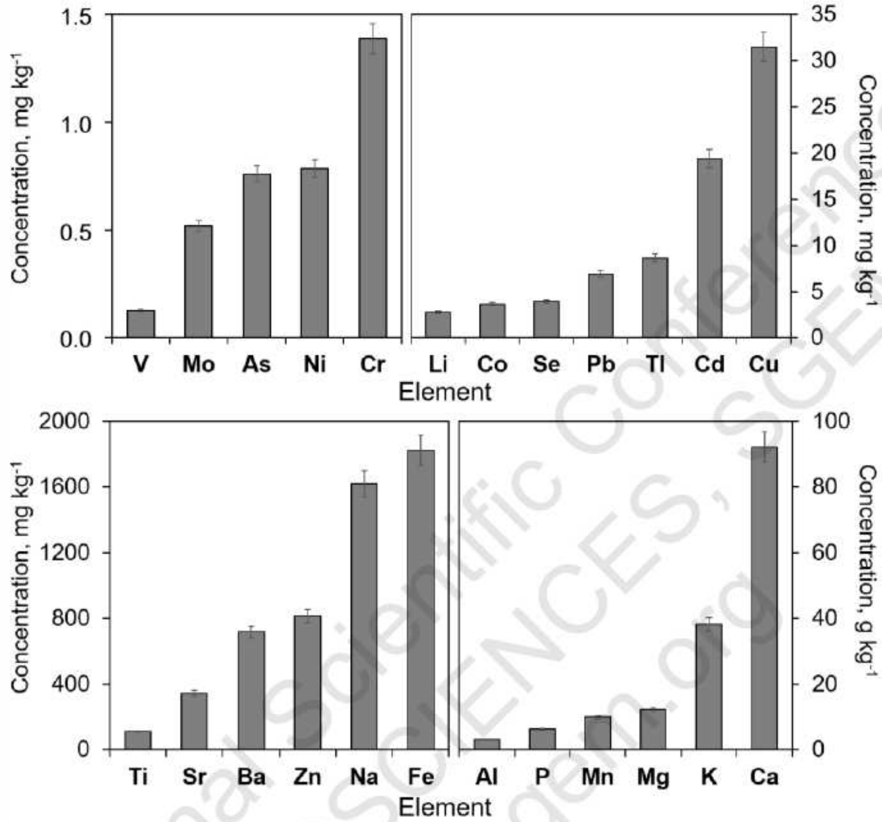

Figure 1. Total concentration of elements in analysed wood fly ash.

Metallic elements and metalloids occur in environment in a form of hydrated ions, insoluble compounds such as carbonates, as well as can be bound with Fe and Mn oxides, organic complexes or incorporated in other chemical compounds. Transfer and bioavailability of elements in environment is strongly dependent on the element speciation [10; 13]. The greatest part of elements (Al, Ba, Cd, Cu, Co, Mg, Mn, P, Pb, Se, Ti, Tl) more than 90% and Zn, Sr, V more than 80% from the total amount were bound in residual fraction indicating their low bioavailability from fly ash (Table 2). Only Cr, K, Mo and Ni were found in water soluble and acid soluble fractions (which are fractions of bioavailable compounds) in considerable amount (>60%). Be and Sb were the elements not detected in any of fractions above the determination levels.

In overall, concentration of heavy metals and metalloids varies greatly in wood ash of various sources and the authors of other studies have reported both lower and higher concentrations than those present in wood fly ash investigated in the current study [15]. Element content of biomass ash is widely variable and dependent on origin and specifics of biomass used as a fuel [14].

Table 2. Distribution of elements by fractions (values in bold indicate element abundance above 60% in a fraction; n. – element was not detected).

Element	Distribution of elements by fraction*, %			Element	Distribution of elements by fraction*, %		
	1	2	3		1	2	3
Al	0.30	0.92	**98.78**	Mn	n.	3.52	**96.48**
As	15.10	n.	**84.90**	Mo	**100.00**	n.	n.
Ba	1.03	5.20	**93.76**	Na	39.85	9.84	50.31
Be	n.	n.	n.	Ni	36.50	**63.50**	n.
Ca	16.89	19.52	**63.59**	P	0.08	2.66	**97.26**
Cd	n.	9.81	**90.19**	Pb	0.79	n.	**99.21**
Co	n.	3.92	**96.08**	Sb	n.	n.	n.
Cr	**76.14**	23.86	n.	Se	n.	6.35	**93.65**
Cu	0.12	1.72	**98.16**	Sr	9.44	10.00	**80.56**
Fe	n.	0.02	**99.98**	Ti	0.05	0.11	**99.84**
K	**60.76**	15.96	23.28	Tl	n.	4.03	**95.97**
Li	9.48	9.29	**81.23**	V	n.	n.	**100.00**
Mg	0.10	10.16	**89.73**	Zn	1.83	11.20	**86.97**

**1: fraction of water soluble compounds; 2: fraction of weak acid soluble compounds; 3: fraction of residues*

In comparison with limits of elements set for ash applicable for utilization in forestry and agriculture in some European countries (Table 3), obtained results indicated that only Cd (19.4 mg/kg) might exceed permitted limit values, while concentration of all other elements was significantly below the proposed limits. However, the limiting values for some elements are widely variable (e.g., for Cd – from 1.5 mg/kg in Finland to 15 mg/kg in Denmark and even up to 30 mg/kg in Sweden) which makes the question to be opened for substantiation why such a great difference exists.

Table 3. Limit values of elements set for wood ash utilization in forestry and agriculture in Europe [15] in comparison to detected values.

Element	Concentration limit values by country, mg/kg			Total average concentration in fly ash detected in the current study, mg/kg
	Denmark	Finland	Sweden	
As	-	25	30	0.76
Cd	15	1.5	30	19.40
Cr	100	300	100	1.39
Cu	-	600	400	31.50
Ni	60	100	300	0.79
Pb	120	100	300	6.95
V	-	-	70	0.13
Zn	-	1500	7000	814.82

In other studies, concentrations of Cd in wood ash have been reported ranging from 1 mg/kg to 28 mg/kg. The effect of cadmium on ecosystems is of particular concern. pH, organic matter and hydrous oxide content are the key factors controlling Cd adsorption into soils. Wood ash with high amount of Cd compounds has reduced risk of this metal leaching, as it bonds with hydrous Mn oxides, through a wide range of soil pH's (Mn is sufficient in studied fly ash samples) and with hydrous Fe oxides. But as it was shown previously in Table 2, it was detected that not less than 90% of Cd were bound in residual fraction indicating its low bioavailability and, therefore, no potential risks should be expected.

Detected total concentration of Al (3 g/kg) and Fe (1.8 g/kg) was considered to be low. Studies done by other researchers have indicated significantly higher content of Al (18-29 g/kg) and Fe (from 13.5 mg/kg to 6.9 g/kg) and, therefore, values of these elements in investigated wood fly ash can be considered as safe [7; 15]. Also amount of Cr and Ni was detected relatively small. Another element of concern Pb that was detected in concentration 6.95 mg/kg should not propose potential environmental risks as the greatest part of it (>99%) is bound in residual fraction which practically indicates the absence of its bioavailability.

CONCLUSION

General properties of fly ash – alkaline pH (>12) and high concentrations of Ca, K and Mg, and also considerable presence of P, Mn and Zn suggest that wood fly ash could be used both, as a liming agent and a fertilizer. However, significant increase in soil pH and salinity (as indicated by electric conductivity of aqueous extracts) in soil is undesirable and may adversely affect plant growth. Wood ash can effectively be used for agricultural purposes of amelioration of acidic soils instead of liming. Therefore, when the calcium carbonate amount of ash is known, it can be used as an effective liming agent. Wood ash could be used to improve nutrient availability and balance nutrient exported by tree harvesting in acid forest soils. Due to the certain nutrient deficiency (like N), use of pure fly ash for soil enrichment is not the most effective. In N-limited soils, wood ash should be applied together with N fertilisers to counteract N immobilisation.

Toxic heavy metal content of wood ash did not exceed the average values compared to the literature data. The greatest part of the elements was bound in residual fraction indicating their low bioavailability and only Cr, K, Mo and Ni were found in water soluble or bioavailable fractions in considerable amount. It indicates possible more or less non-toxic behaviour of these elements and, therefore, this fact is potentially usable for development of fertilizing agents using fly ash.

In addition, agricultural application of wood ash in overall has significant economic importance. Application of ash on agricultural and forest lands may lower the expenses of landfilling ash as a waste and can promote development of 'zero waste' concept.

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