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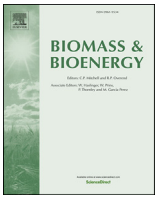

Research paper

Elemental composition of willow short rotation crops biomass depending on variety and harvest cycle

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ABSTRACT

The use of woody biomass in thermochemical conversion is still the most popular method of obtaining bioenergy from this material. Elemental composition has a significant effect on biomass quality and parameters of the combustion process. The aim of this study was to determine the content of selected macroelements (phosphorus, potassium, magnesium, calcium, sodium and sulphur), microelements (boron, copper, iron, manganese and zinc) and trace elements (cadmium, chromium, nickel and lead) in willow biomass of two different varieties and three clones, harvested in annual, biennial and triennial cycles in north-eastern Poland.

The study found significant variability between varieties/clones and harvest cycles. Biomass of the UWM 200 clone of *Salix alba* in triennial harvest rotation had the best parameters as a potential fuel source; it was found to contain the significantly smallest concentrations of P, K, Na, S (1.48, 5.45, 0.08, 0.35 g kg^{-1} DM, respectively) and Fe, Cr, Pb (208.85, 4.91, 0.83 mg kg^{-1}, respectively). The content of all of the elements under study decreased significantly with an extended harvest cycle, and the differences, when comparing the triennial to the annual cycle, ranged from −9% to −29% for macroelements, from −7% to −48% for microelements and from −11% to −20% for trace elements.

1. Introduction

Wood biomass has been used by humans as fuel since prehistoric times and it accounts for 6% of all energy sources globally [1]. It is estimated that more than 2 billion people in developing countries depend on wood for heating and cooking, which shows that wood energy is mostly used on a non-commercial basis [2]. However, since resources of the main energy feedstock, such as coal and oil, are becoming exhausted and because of the global policy of reducing CO_2 emission, woody biomass has been increasingly often consumed in energy generation for industry, where it can be used traditionally to produce heat and electricity by combustion, gasification, but also – owing to its rich chemical composition – it has enormous potential in the chemical industry and biorefineries [3,4].

One source of biomass are lignocellulosic plants, such as willow, grown in short rotation (short rotation crops, short rotation woody crops or short rotation forestry) depending on the harvest cycle, usually 1–7 years [5,6]. It has been shown in numerous studies of willow plantation productivity that extending the harvest cycle increases the yielding potential and growth in 3- or 4-year harvest cycles is among the optimum solutions [7–9].

Woody biomass is used mainly in combustion processes [10]. One of the greatest advantages of biomass is the possibility of co-firing with coal in combustion installations, originally designed only for coal. However, it should be stressed that co-combustion of biomass with coal is one of the worst methods of its use as fuel, especially when the process is conducted in installations designed for burning coal, which lowers the effectiveness of using the energy contained in biomass. It must be emphasized that biomass provides much less energy per unit than good quality coal, but the environmental benefits of co-firing (i.e. reducing CO_2 emissions) still makes this source of energy very attractive [11,12]. Furthermore, when it comes to the content of ash as a product of incomplete combustion, the biomass of SRWC can contain several times less ash than biomass of straw or grass [13] and up to a dozen times less compared to coal [14].

However, major ash-forming elements like Al, Ca, Fe, Mg, K, Na, P, Si, Ti; volatile minor elements like As, Cd, Hg, Pb, Zn and partly or non-volatile elements like Ba, Co, Cr, Cu, Mo, Mn and V are the

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cause of ash melting, corrosion, aerosol emissions and they are of crucial importance in the choice of an ash utilisation method [15]. Ash from biomass burning can be a valuable agent used to improve soil properties in growing many plant species and - when combined with other fertilisers - they can have a beneficial effect on the productivity of crops [16,17]. However, the more macro-, micro- and trace elements in biomass, the more ash remains from burning and, consequently, less energy can be obtained from a unit of biomass.

Compared to coal, biomass can contain higher concentrations of Mn, K, P, Ca, Mg, Na and the elemental composition of biomass can be affected by such factors as plant species, geographic location, age of the plants and fertilization and pesticides used in cultivation [18]. It is a well-known fact that extending the harvest cycle reduces the content of chemical elements in woody biomass per mass unit, which is associated with a higher content of the elements in bark than in wood and the bark/wood ration increases with extending the harvest cycle because of the growing diameter of shoots [19,20]. Variability of the content of chemical elements in biomass of different willow clones has been observed in earlier studies [19,21]. It has been shown that a large biomass yield of relatively high energy value was obtained from the varieties under study [22].

It is important to know the elemental concentration in high-yielding varieties because plant varieties of the best biomass quality parameters should be used for SRWC plantations whose biomass will be used in thermal conversion, which will help to reduce the negative impact on combustion furnaces and power boilers. Therefore, considering the variability of the chemical composition, demonstrated by other researchers, which depends on such factors as variety/clone, local habitat conditions and harvest cycle, it is important to seek a combination of these factors which will prove optimal for growing willow as an energy crop.

Therefore, the aim of this study was to determine the content of selected macroelements (P, K, Mg, Ca, Na, S), microelements (B, Cu, Fe, Mn, Zn) and trace elements (Cd, Cr, Ni, Pb) in willow biomass of two different varieties and three clones harvested in annual, biennial and triennial cycles in north-eastern Poland.

2. Materials and methods

2.1. Description of the experiment

The study was based on an exact, two-factorial experiment with willow coppice, located in the north of Poland in the Kwidzyn Lowlands in the village of Obory (53°43′ N, 18°53′ E), conducted from 2003 to 2006. The experiment was located on humus alluvial soil, classified as—Mollic Fluvisols, which is the optimal soil for willow cultivation. Analysis of 3 levels of soil horizon (0−37, 37−78 and 78−150 cm) showed that soil was originated from silty clay. In all layers of the soil, pH (in H_2O) was slightly alkaline, from 7.4 to 7.8. Bulk density was in the range from 1,19 Mg m^{-3} in the top soil horizon through 1.35 to 1.28 Mg m^{-3} in subsoil layers. The main parameters of top soil horizon were: content of $CaCO_3$ (5.90 g kg^{-1}); total N content (2.97 g kg^{-1}) and content of available forms of potassium, magnesium and phosphorus (204.8, 154.1 and 153.5 mg kg^{-1}, respectively). Before trial establishing, the experimental site was managed according to good agricultural and environmental practices, without introducing any of hazardous contaminants. No mineral fertilisers were applied in the year when the experiment was established. The following doses of fertilisers were sown manually in the subsequent years of the experiment N − 90 kg ha^{-1}, P − 18 kg ha^{-1}, K − 66 kg ha^{-1}.

The first factor examined in the experiment were two willow varieties and three clones, all of which were cultivated by the University of Warmia and Mazury in Olsztyn: clones UWM 200 and UWM 095 (both of the *Salix alba* L. species), varieties Tur, Turbo and clone UWM 046 (all of the *Salix viminalis* L. species). The other factor was the harvest cycle: every year, every two years or every three years. Detailed information about setting up and running experiment is provided in a previous research article by Stolarski et al. [22].

2.2. Sampling procedure

One and two-year old plants were harvested after the 2005 vegetation period and three-year old plants after the 2006 vegetation period.

Willows were harvested manually with a blade trimmer powered by a combustion engine. During the harvest, representative plant stems were collected from each plot to determine chemical characteristics.

2.3. Laboratory analyses

Potassium, calcium and sodium were assayed by flame photometry. Samples were mineralised in H_2SO_4 and, subsequently, the intensity of radiation was measured which was emitted by ions of a given element formed when the solution was sprayed in the photometer flame (C. Zeiss Jena). The content of phosphorus and boron was determined by colorimetry on a Specol colorimeter. In order to determine the phosphorus content, samples were mineralised in H_2SO_4, followed by measurement of the deposit colour formed after the reacting mixture ($HNO_3 + NH_4VO_3 + (NH_4)6Mo_7O_{24}$) was added. In order to determine the content of boron, samples were mineralised in a muffle furnace at 500 °C, the post-mineralisation residue was dissolved in HNO_3 and diantrimide was then added and the colour intensity was measured. Sulphur was assayed by nephelometry on a Specol colorimeter. Samples were mineralised in a muffle furnace at 500 °C, the post-mineralisation residue was dissolved in HNO_3, $BaCl_2$ was added and the turbidity was measured. Magnesium, copper, iron, manganese, nickel, lead, cadmium and chromium content were measured by atomic absorption spectrometry (AAS). For the magnesium assay, samples were mineralised in H_2SO_4, whereas samples for the other assays were mineralised in a mixture of acids: HNO_3 and $HClO_4$ (4:1). Subsequently, absorption of radiation by ions was measured when each solution was sprayed in the flame.

The analyses were carried out in three replications. The concentrations of all elements in the study are presented on dry matter.

2.4. Statistical analysis

The results of the tests were analysed statistically using STATISTICA 9.1 PL. The mean arithmetic values, Pearson correlation coefficients and standard deviation of the examined features were calculated. Homogeneous groups for the examined characteristics were determined by means of Tukey's HSD multiple comparison test with the significance level set at $P < 0.05$.

3. Results and discussion

3.1. Macroelements in willow biomass

The content of macroelements in willow biomass was significantly differentiated by varieties and clones as well as by harvest cycles (Table 1; Fig. 1; Fig. 2). The UWM 200 clone had the lowest mean content of P and K (1.76 and 6.99 g kg^{-1} DM, respectively) (Fig. 1), but the K content in an annual harvest cycle was