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The content and emission factors of heavy metals in biomass used for energy purposes in the context of the requirements of international standards

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ABSTRACT

The aim of this work was to study the content of seven heavy metal factors within different biomasses. The potential environmental effects associated with the release of these elements into the atmosphere were also studied by determining the emission factors for each of biomass. 31 samples of biomass which were classified into four groups, i.e.: wood biomass, herbaceous biomass, fruit biomass and aquatic biomass and analyzed with use of ICP-OES spectrometer. Performed results were analyzed in the context of the requirements of international standards, described in the EN ISO 17225:2014. Higher heavy metal contents than the limits described in the EN ISO 17225:2014 standard were detected within some of the studied biomass samples. Importantly, this is also related to the products available on the market, i.e., wood pellets or wood chips. Among the detected trace elements, the largest limit exceedance was for lead (wood chips from a rubber tree, pomace oil and palm kernel shells) and arsenic (Sea Balls). The highest emission factors were determined for the herbaceous, fruit and aquatic biomass. However, the wood chips studied were characterized by relatively high emission factors for each heavy metal. A comparison of the emission factors calculated for the studied biomass samples and for coal revealed that the total emission of heavy metals during the combustion of wood pellets and wood chips was lower than that calculated for hard coal.

1. Introduction

The combustion process is one of the main sources of emissions of environmentally harmful chemicals such as sulfur and nitrogen oxides, halogens, volatile organic compounds and trace elements. During combustion, the trace elements present in fuel in the form of stable chemical compounds remain in the ash. Regarding less stable compounds, the elements decompose and are carried away from the process gases in the form of vapor or in combination with fly ash [1]. These compounds include key elements contaminating the environment, such as arsenic, cadmium, manganese, copper, nickel, lead, chrome and zinc, usually termed heavy metals. Their impact on the environment and living organisms is clearly harmful [2–4]. They pollute aquatic ecosystems and soil and act in a manner that is deleterious for living organisms [3,5–7]. The most toxic trace elements are cadmium and lead [8,9]. Cadmium adversely affects the excretory, respiratory and circulatory systems of living organisms. A high lead content in a living organism poisons the digestive and nervous systems. Lead is carcinogenic and mutagenic, similar to zinc, which also causes anemia. Other heavy metals also adversely affect living organisms. Chromium compounds damage the digestive system, cause skin lesions and are mutagenic, embryotoxic and teratogenic. Arsenic poisoning can lead to death due to a reduction in the activity of enzymes necessary for the proper functioning of the organism and also causes neurological disorders. The toxic effects of arsenic, cadmium, lead and chromium may be additive or suppress each other upon simultaneous exposure to these elements, depending on the type of interaction and the organ or system in which the interaction occurs [10]. Copper is widespread in many living organisms, but its excess can lead to eating disorders and liver damage. A high concentration of nickel causes skin allergies and shortness of breath [11]. The concentration of trace elements in plants is very diverse in the environment depending on the

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species and varieties of plant and the vegetation conditions [12,13]. Trace elements can be present in plants as complex organic compounds, such as metal oxalates, inorganic compounds, such as sulfides or oxides, or in elemental form. The trace elements present in plant biomass can be essential for the functioning of the plant, including iron, copper, manganese, zinc, and cobalt, or toxic to the plant in even small quantities, such as lead, cadmium, antimony, mercury and arsenic. The main sources of the trace elements contained in plant biomass are minerals and fertilizers in the soil and dissolved in water [14]. Plants primarily absorb these elements through their root system and, to a lesser extent, their leaf blades. For some elements, e.g., cadmium, the organic acids secreted by roots (e.g., citric, oxalic, acetic, tartaric, fumaric) play an important role in the uptake from the soil. Elements such as copper, zinc, and cadmium may also be absorbed through the leaves from atmospheric dust and precipitation rain. Hence, one can expect an increased concentration of these elements in the biomass growing in areas of industrial facilities (e.g., power plants, steel mills, coke plants) [15–18].

The problem regarding heavy metal emissions mainly depends on the content of the individual elements in the fuel, the conditions of the combustion process, the applied flue gas cleaning systems, and the propensity of the elements to volatilize, which is primarily associated with the nature of chemical bonds between the elements present in the fuel [19]. During the combustion process, trace elements contained in fuels, including biomass, are released from the combustion zone in the gaseous form or as condensate on the surface of particulate matter (fly ash) [20]. Trace elements are characterized by varying degrees of volatility (Fig. 1).

Approximately 70–90% of heavy metals present in fuel pass to fly ash during the combustion process [1,2,20–23]. The mechanism of the behavior of the trace element vapor in the combustion process is complex. Emission of the elements depends on the design of the boiler, working conditions, exhaust gas cleaning system, and the properties of the burned fuel. Because most of the trace elements are a component of the released dust, the best way to reduce such emissions is through the use of high efficiency dust collectors, such as electrostatic precipitators (ESP) or fabric filters (FF). The volatile metals can also condense to submicron particles of fly ash in the form of an aerosol. These particles are difficult to precipitate onto the dust filters, and, as a result, the aerosols can pose environmental and health hazards due to their emissions with the flue gases [24]. Application of heated filters increases the degree of removal of certain trace elements [20].

Large power boilers used in massive power plants are equipped with air protection systems that meet the requirements of the Best Available Technology (BAT) and greatly reduce the amount of dust and trace elements emitted into the air. However, the threat of pollution remains for municipal energy facilities that use only mechanical dust collectors (cyclones) [1]. In Poland, the communal energy sector represented by households or small local power plants composes a significant share of the total emissions of trace elements [24]. Given the need to reduce the emissions of pollutants into the environment from power generation and heating systems, fossil fuels are being replaced with varying degrees of biofuels derived from plants. Biomass is an indigenous source of energy that is available in most countries, even if they do not possess any natural fossil fuel resources, and may also ensure economic growth and employment, particularly in rural areas. Biomass application may diversify according to the available energy development techniques, which may lead to a more secure energy supply. The energy content of biomass (on a dry, ash-free basis) is similar for all plant species, in the range of 17–21 MJ/kg [20,25]. According to the provisions of the Kyoto Protocol, in 2020, biomass is expected to make a key contribution to 20% of the total EU's renewable energy target [26]. Currently, this fuel serves as much as 8–15% of the world's energy resources [27]. In Poland, biomass for energy purposes is obtained primarily from forest residues, waste from the timber and agro-food industries, public utilities and agriculture. Waste biomass is also imported from abroad. The content of trace elements in biofuels depends on the type of biomass and the cultivation conditions and location.

Quality requirements for solid biofuels, including limits on the contents of trace elements are described in a series of standards, EN ISO 17225 [28–33], and are presented in Table 1.

The standards criteria arise from the ever-increasing requirements aiming to reduce the emissions of these elements into the environment. This is of particular importance in the case of low-energy capacity boilers, due to the relatively poor control systems and lack of exhaust gas cleaning systems, especially in residential neighborhoods. These criteria are necessary in the case of power plants because of the scale of biomass used.

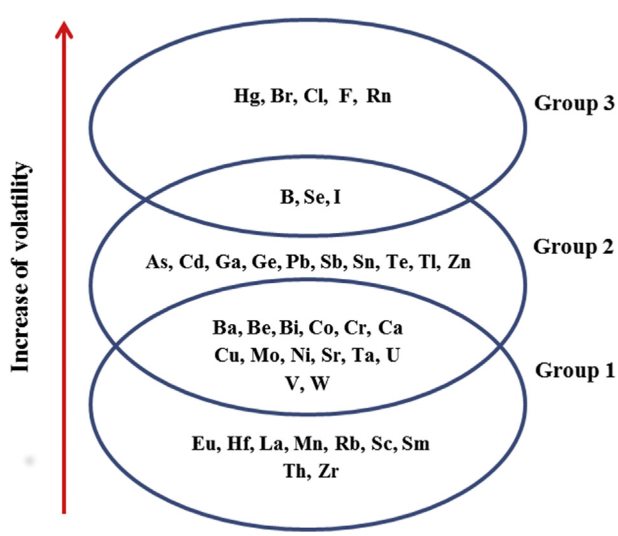

Fig. 1. Volatility of trace elements during fuel combustion and gasification [22]. Group 1: Elements approximately equally distributed between the bottom ash and fly ash, or show no significant enrichment or depletion in the bottom ash. Group 2: Elements enriched in the fly ash and depleted in the bottom ash, or show increasing enrichment with decreasing fly ash particle size. Group 3: Elements totally emitted in the vapor phase.

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