



## Research paper

# Bioavailability of nutrients and harmful elements in ash fertilizers: Effect of granulation



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## ARTICLE INFO

## Article history:

Received 8 June 2016

Received in revised form

14 March 2017

Accepted 19 March 2017

## Keywords:

Fly ash

Granulation

Fertilizers

Leaching

Waste utilization

## ABSTRACT

Environmental policies of the European Union (EU) aim to increase the amount of renewable energy and to improve the use of waste streams. This will increase the amount of fly ash (FA) from biomass combustion, thereby increasing the need for its utilization. Biomass FA is a good fertilizer since it contains most of the nutrients that plants need. Sequential leaching would provide a more accurate assessment of the potential bioavailability of the harmful elements and nutrients than the pseudo-total and/or water-soluble concentration analysis that EU environmental legislation typically requires. This study investigated the effect of granulation and ammonium sulfate addition on the solubility and bioavailability of nutrients and harmful elements from peat and wood co-combustion FA by using sequential leaching and pseudo-total acid digestion. The recoveries of the easily bioavailable nutrients Ca, K, Mg, P, and S as well as the total bioavailability of Ca, K, Mg, and S reduced significantly after granulation. Therefore, granulation reduced the fertilizing effect of FA. The pseudo-total recovery of Ca, Mg, and S reduced after granulation, indicating that these types of FA form some very stable silicate compounds besides the common self-hardening products. Ammonium sulfate addition increased the recoveries of the easily bioavailable nutrients and total bioavailability recoveries of the Ca, K, and Mg back to the same levels as those in FA. The total bioavailability of the harmful elements As, Cd, Cr, Cu, Ni, Pb, and Zn was very low, and this does not limit the usability of FA as a fertilizer.

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## 1. Introduction

One of the main priorities of the EU growth strategy (Europa 2020) is sustainability, which forms the basis of a low-carbon economy [1]. A low-carbon economy is achieved through reductions in greenhouse gas emissions and increases in both renewable energy sources and energy efficiency. The aims of the EU circular economy strategy are to increase recycling and re-use of products and waste materials [2]. The EU Waste Framework Directive (2008/98/EC) [3] includes a 5-step waste hierarchy, which describes the different options available for dealing with the waste. The first goal of the waste hierarchy is the prevention of waste streams. If this is not possible, the next step down the hierarchy is the preparation of waste for re-use, followed by recycling and other recovery (e.g., energy recovery), and finally, if none of the initial 4

steps are feasible, waste should be disposed of by ecologically beneficial methods.

The forest and power industries produce large amounts of fly ash (FA) every year in Europe. A large part of this ash ends up at waste disposal sites, even though it could be productively utilized. Changes to the legislation, the Europa 2020 growth strategy, and the EU circular economy strategy have increased the need to utilize different combustion ashes. The most natural way to utilize biomass-based FA is to use it as a fertilizer or soil amendment. In particular, wood FA contains all the macronutrients plants need in almost the correct proportions, excluding nitrogen (N), which is released into the atmosphere during combustion [4]. In peatlands, nitrogen levels are usually naturally high, whereas phosphorous (P) and potassium (K) are the growth-limiting nutrients. Therefore, FA has great potential as fertilizers for use in peatland forests. It has in fact been shown that FA can outperform commercial PK fertilizers for improving tree growth [5] as well as the financial performance of forest management on peatlands [6].

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In Finland, to prevent dust problems, FA has to be granulated before application on fields or forests. Granulation is known to be a significantly more cost-effective alternative for ash recycling compared with unprocessed FA mainly due to improved logistics [7]. Co-granulation of FA with some nitrogen containing material such as hygienized sewage sludge could produce new fertilizer products to nitrogen poor soils [8].

The EU environmental legislation typically requires that the pseudo-total concentrations (i.e. acid-leachable metals that are not part of silicate matrix) and/or water-soluble concentrations of the harmful elements be studied from waste and residue materials [9–12]. This does not give an accurate representation of the environmental risks associated with the utilization or disposal of these materials. From an environmental point of view, of utmost importance is not the total concentration in wastes and other residues, but rather the ease with which the metals can be mobilized into the environment and their bioavailability. The water-soluble concentration is not a sufficient measure of the environmental risks because distilled or deionized water used in these tests does not represent the normal salt concentration or the ionic strength of the soil solution. Further, rainwater is usually clearly acidic nowadays. The water-soluble concentration measures only the instantly bioavailable fraction of the contaminants and does not evaluate the potential of contaminants to become more available with time [13,14]. Moreover, these procedures are not sufficient to assess the bioavailability of nutrients from FA-based fertilizers. Therefore, to obtain more detailed information about the effect of environmental conditions on the bioavailability and mobility of different contaminants, sequential leaching has been widely used with different environmental samples over the past decades [15].

In the sequential leaching procedure, various types of increasingly severe chemical reagents are applied to the sample; this procedure divides the total extractable metal concentration into fractions in order to assess the bioavailability and the form in which the metals occur in a waste material. Therefore, compared to the pseudo-total concentrations, the sum of the fractions can give a more accurate assessment of the potential total bioavailability of the harmful elements. Sequential leaching does not necessarily mean total decomposition, and the cumulative extractable recoveries are usually clearly lower than the total concentrations.

In this study, the effect of granulation and ammonium sulfate addition on the solubility and bioavailability of nutrients and heavy metals from peat and wood co-combustion FA was studied using the sequential leaching procedure and pseudo-total acid digestion. Although granulation is a standard procedure to improve the handling of FA-based fertilizers, such a study has not been implemented before.

## 2. Materials and methods

### 2.1. Raw materials and granulation

The FA used in this study was from a 96-MW thermal power plant situated in Rovaniemi, Northern Finland. The power plant uses a circulating fluidized bed combustion technique. The fuels used at the plant are wood and peat. The fuel ratios (dry mass) at the power plant were approximately 50% wood (logging residue) and 50% peat. The sample was collected 14.5.2014 directly from ash silo. Commercial  $350 \text{ g} \cdot \text{L}^{-1}$  ammonium sulfate solution (Envor, Finland) was used in the granulation process of granule FAGR2 (see below).

The compositions and sample names of the FA granules used in this study are presented in Table 1. For each granule type, a few kilograms were produced. Granule FAGR1 contained only FA and

water, whereas granule FAGR2 also contained ammonium sulfate solution. While agitating the FA using a ribbon blade agitator, water (and ammonium sulfate solution) was slowly added to the FA until small aggregates started to form in the paste. The pastes were granulated using a simple pan granulator. A very strong odor of ammonia was observed during FAGR2 granulation. The granules were cured in a hot air oven at  $50 \pm 2 \text{ }^\circ\text{C}$  for 24 h and stored at room temperature ( $21 \text{ }^\circ\text{C}$ ).

### 2.2. Sequential leaching procedure

The pseudo-total element concentrations were characterized by aqua regia digestion according to standard ISO 11466 [16] and analyzed with the ICP-OES technique. The 4-step sequential leaching procedure used in this study is presented in Table 2. This procedure is based on the Community Bureau of Reference (BCR) procedure [17]. Stages 2–4 follow the BCR procedure, but the first stage involves extraction with deionized water acidified to pH 4 with  $\text{HNO}_3$  [18]. The purpose of the first stage is to simulate the effect of acidic rainwater – present day rain – on the solubility of the metals. This 4-step sequential leaching procedure has been used successfully with samples including bottom ash and FA [18–21].

The sample mortars were first crushed and sieved to particle sizes smaller than 0.5 mm. The eluates from each step were separated from the residue by centrifuging for 20 min ( $\text{RCF} = 3000$ ) and analyzed using the ICP-OES technique. Duplicate samples from each batch were analyzed, and the averages were calculated. The moisture contents of the FA and the FA granules were measured according to standard SFS-EN 12880 [22] by drying the samples in a hot air oven for 24 h at  $105 \pm 2 \text{ }^\circ\text{C}$ . The dried samples were placed in cooling desiccators and weighed. However, the samples were not dried prior the sequential leaching procedure, since heat can affect the leaching of elements [23]. Instead, the moisture contents were taken into account as the leaching results were calculated. The moisture mass fractions of the samples were low: 0.42% for FA; 1.62% for FAGR1; and 1.55% for FAGR2.

The fractions of the 4-step sequential leaching are the water-soluble fraction; exchangeable and acid-soluble fraction; reducible fraction; and oxidizable fraction [15]. In theory, the first fraction should contain water-soluble ions. This fraction is the most mobile, and it contains potentially the most readily available metal and metalloid species. The second fraction should contain metals bonded electrostatically, metals bonded with weak covalent bonds, or metals bonded to carbonates. The third fraction should contain metals bonded to Mn and Fe oxides, and the fourth fraction metals bonded to organic matter or to different sulfides and oxides. However, it should be noted that sequential leaching was originally designed for fractionating of sediments. Therefore, the bonding of different metals originating from matrixes that differ notably from sediments, such as FA, cannot be deduced precisely from the sequential leaching results. For example, FA is quite basic, and the acetic acid used in the second step of sequential leaching is not strong enough to acidify the sample matrix. Thus, even if the FA matrix contained some carbonates, they would not dissolve. Furthermore, the reagents used in the sequential leaching are not completely target specific. However, even when the bonding of metals cannot be deduced from sequential leaching data, it still gives a good estimate of the solubility of metals in real environmental conditions. In the present study, the first two fractions (F1 and F2) are referred to as easily bioavailable fractions. The total bioavailability refers to the sum of the fractions (F1–F4) [15,17,24]. Recovery % of a particular element E was calculated with equation (1):

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