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Phosphorus and cadmium availability in soil fertilized with biosolids and ashes

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HIGHLIGHTS

- Fuel additives were used to increase phosphorus availability in ash.
- Cd/P ratios in ash were 2–5 times lower than in biosolids.
- Fuel type and combustion temperature had little effect on Cd and P uptake by plants.
- Ash increased biomass more effectively than biosolids.

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ABSTRACT

The recycling of hygienized municipal sewage sludge (biosolids) to soil as the source of phosphorus (P) is generally encouraged. The use of biosolids, however, has some concerns, such as the presence of elevated concentrations of potentially toxic trace elements, and the possible presence of pathogens, hormones and antibiotics. Organic substances are destroyed during combustion whereas trace elements could partly be separated from P in different ash fractions. Biomass combustion waste (ash) can instead be considered as an alternative P source. This study evaluates and compares the impact of biosolids and their combustion residues (ashes), when used as fertilizers, on P and Cd solubility in soil, plant growth and plant uptake of these elements. Biosolids were also amended with K and Ca to improve the composition and properties of P in ashes, and incinerated at either 800 °C or 950 °C. Combustion of biosolids improved the Cd/P ratio in ashes by 2–5 times, compared with the initial biosolids. The low Cd content in ashes (4–9 mg Cd $(\text{kg P})^{-1}$) makes this material a particularly attractive alternative to mineral fertilizers. Significantly higher pore water P (as well as total N) was measured in soils containing biosolids, but plants produced a higher biomass in soil fertilized with ashes. The K and Ca amendments prior to biosolids combustion generally decreased the total Cd in ash, but had little effect on P and Cd uptake and biomass growth. Similarly, the combustion temperature had negligible effect on these factors as well.

1. Introduction

Organic waste, such as wastewater or sewage sludge, is a source of valuable nutrients (nitrogen, phosphorus, carbon), which are essential for soil ecosystem functioning. Currently, the recycling of hygienized municipal sewage sludge (biosolids) to soil as the source of nutrients is encouraged in Sweden (Swedish EPA, 2002). The application of such materials on arable land includes both benefits and risks and might be seen as an additional pollutant source. To avoid an irresponsible application of biosolids and consequent contamination of arable soils, the regulation of trace element content in biosolids is enforced by national legislation and established limit values, e.g. for Cd in Sweden it is 750 mg $(\text{ha y})^{-1}$ soil

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application or 2 mg (kg dw)$^{-1}$ of biosolids (Swedish EPA, 2001).

One of the largest benefits of using biosolids is the supply of phosphorus (P) to crops, which is assumed to be in a more plant available form than P in mineral fertilizers. However, sewage sludge is considered to be an important contributor of cadmium (Cd) to arable land (Eriksson, 2000; Bergkvist et al., 2003). Nevertheless, commercial mineral P fertilizers also contain trace elements, especially Cd. Cadmium concentration in P-based mineral fertilizers range between 0.3 and 100 mg kg^{-1} (Roberts, 2014), which is substantial compared to the total Cd concentration in soil (0.01–2.7 mg kg^{-1}) (Kabata-Pendias, 2001). Cadmium is a toxic element without known biological function in higher organisms, therefore, even in low concentrations Cd may cause toxic effects to humans (WHO, 1992). Cadmium in food and drinking water are the main sources of human exposure to this element (Nordberg, 2009; Satarug et al., 2010). Osteoporosis, the disease affecting over 200 million people worldwide (Kanis, 2007), has been linked to increased Cd in the environment and its intake with food (Staessen et al., 1999).

The use of biosolids has other concerns as well, such as the possible presence of pathogens, hormones and antibiotics. This is one of the reasons why it is difficult to accept biosolids as forest fertilizers in Sweden. In contrast, biofuel ashes, a waste material generated during the combustion of biomass, are encouraged to be used for forest fertilization (Swedish Forest Agency, 2008). Ashes are rich in valuable nutrients such as P, K and Ca. A well-performing combustion destroys pathogens and problematic organic molecules, but potentially toxic elements, including Cd, might accumulate in the nutrient-rich ash fraction. Redistribution of elements into desired ash fractions can be achieved by varying system parameters such as temperature (Van de Velden et al., 2008). By this, the amount of Cd can be reduced in certain ash fractions while retaining P. Furthermore, enrichment of biosolids with combined potassium (K) and calcium (Ca) prior to combustion might prevent the formation of highly stable and poorly soluble calcium phosphates that often dominate in ash (Skoglund et al., 2014). Consequently, the incorporation of P into structures such as $Ca_9KMg(PO_4)_7$ or $CaKPO_4$ during the combustion process might generate similar P solubility and availability in ash as that in biosolids. If the Cd content in ash in relation to P is low, ash can become a suitable source of P (and alternative to mineral P sources) for fertilizing arable land without any need for further ash treatment.

This study aimed at evaluating and comparing the impact of biosolids and their bed ash recovered after bubbling fluidised bed combustion, when used as fertilizers, on P and Cd solubility in soil, plant growth and plant uptake of these elements. This study is a part in a series of articles describing the potential of biosolids combustion with the intent to improve phosphate properties in ashes by modifying fuel composition (Skoglund et al., 2014).

2. Material and methods

2.1. Biosolids and ashes

Biosolids originated from municipal wastewater treatment plants in Umeå and Skellefteå municipalities, Sweden, which used the precipitation agents $Fe(II)SO_4$ and polyaluminiumchloride, respectively. Biosolids were made from digested wastewater treatment sludge by pelletizing and drying at 110 °C. Additional samples were prepared by amending the biosolids with K_2CO_3 (K_2CO_3 >98%, Fisher Scientific) or a combination of K_2CO_3 and $CaCO_3$ ($CaCO_3$ >98%, Fisher Scientific) to adjust the contents of K and Ca and obtain the molar K/P ratio of 1: 1 and K/Ca/P of 1:1:1, respectively. These molar ratios were chosen to simulate the effect of co-combustion with biomass on phosphate speciation in the resulting ash fractions. More details on fuel preparation and raw materials are given in Skoglund et al. (2014). Total solids and loss on ignition of the biosolids were measured following the Swedish Standard (SS 02 81 13, 1981).

All three types of biosolids were combusted in a bench-scale bubbling fluidized bed reactor for a maximum of 75 min at either 800 °C or 950 °C. These temperatures were selected to simulate co-combustion scenarios with agricultural residues or straw-based energy crops (800 °C) and woody-type waste streams or energy crops (950 °C) and to determine phosphorus recovery potential from ash by reducing the amount of potentially harmful elements associated with phosphates. The bed ash particle fraction >1.2 mm was collected for further analyses and experiments since this could be a suitable size fraction to recover from full-scale processes. Modified EPA methods 200.7 (US EPA, 1994a) and 200.8 (US EPA, 1994b) were used for the total element composition analysis with ICP-AES/SFMS. All analyses were run in triplicates. The list of samples and abbreviations used in the text are given in Table 1.

Easily soluble (available) phosphorus (P–AL) in biosolids and ashes was extracted according to Swedish Standard (SS 02 83 10, 1993). Briefly, 5 g of the materials were mixed with 100 ml of extraction solution (0.1 M ammonium lactate and 0.4 M acetic acid), shaken for 90 min and filtered immediately through a paper filter and within two days analysed with ICP-OES.

2.2. Soil and pot experiment

Soil was collected in a coniferous forest in Northern Sweden below the humus layer, air dried, homogenized and sieved to a <4 mm fraction. Total solids and loss on ignition were measured following the Swedish Standard (SS 02 81 13, 1981).

The soil was mixed with 2.5 dwt% either biosolids or ashes. One kg of each mixture was placed in plastic pots in triplicates and sown with 1.5 g of a grass/seed mixture supplied by Veg Tech AB, Vislanda, Sweden. The mixture contained 90% grass seeds and 10% herb seeds and is intended for re-vegetation of sandy soils. A control sample without any fertilizing material was prepared in the same manner. The soil was moistened to reach 20 wt% humidity level. The pots were stored in a laboratory under an artificial light (12 h on, 12 h off), holding constant soil moisture level by manual irrigation with distilled water. The pots were equipped with Rhizon soil moisture samplers (5 cm long, 2.5 mm in diameter, 0.15 μm pore size; Eijkelkamp, the Netherlands).

Soil pore water was sampled twice: the second day after placing soil in pots and 7 weeks later during the plant harvest. Pore water samples were collected in vacuumed 100 ml glass bottles and used for measuring pH and electrical conductivity (EC), analysis of elements with ICP-OES (Perkin Elmer Optima 2000V), and concentrations of PO_4–P, SO_4^{-2}, Cl^-, NO^{-3}, NH_4–N and the total N using spectrophotometer (QUAATRO, Bran + Luebbe).

The aboveground plant parts were harvested ca 1 cm from the soil surface, washed with double distilled water, dried at 50 °C for 72 h, weighed for dry mass determination, then ground using a stainless steel grinder and analysed for element composition by the accredited laboratory ALS Scandinavia. Certified reference material NIST 1547-Peach Leaves was used for quality control of plant extractions. Besides extraction and instrument blanks, quality control standard solutions were run periodically between the samples.

2.3. Statistical analyses

Analysis of variance (ANOVA) and regression analysis was applied using the software *Statgraphics Plus 5.1.* A two-sample t-test ($p < 0.05$) was used to differentiate between the sample means. Multivariate data analysis (MVDA) was performed using *SIMCA-*