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Original Research

Cattle Horn Shavings as Slow Release Nitrogen Fertilizer

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Abstract

An investigation of the chemical composition of cattle horn shavings produced in Lithuania was conducted. The horn shavings were found to consist of 86.62% dry matter, 99.16% organic matter, 39.97% organic carbon, 15.54% N (99.52% of it was in slightly soluble organic compounds), 0.165% P, 0.396% Ca, 0.09% K, 0.049% S, 0.014 % Mg, 6.68 mg kg^{-1} Cu, 118.0 mg kg^{-1} Zn, and traces of heavy metals Cr, Pb, and Cd. Elements Ni and Hg were not found in the tested samples. pH value of horn shavings was 7.2. Ammonium nitrogen (NH_4–N) was a prevailing soluble nitrogen compound in the tested samples. The predominant size of horn shavings was within the range of 0.5-2.5 mm (90% of total weight). Our research evidence on the rate of release of water-soluble nitrogen compounds suggests that cattle horn shavings are suitable for use as slow release nitrogen fertilizer. Mineral nitrogen compounds are gradually released from the cattle horn shavings incorporated into soil, thus supplying the plants with nitrogen during the whole growing period.

Keywords: horn shavings, chemical composition, slow-release fertilizers

Introduction

An issue of utilization of by-products and/or waste products of animal and plant origin produced in agricultural, processing, and other sectors of the economy is drawing more attention nowadays. Part of these products, i.e. animal hair, hoofs, and feathers contain keratin. Such waste products cause environmental problems, on the other hand they are raw materials required for producing new products [1]. Keratin is not soluble in water or in weak acid/alkaline solutions, thus it takes a number of chemical processing steps in order to extract keratin from the raw material [2]. Due to this fact simpler ways to process and/or to utilize the keratin containing waste products are being sought. An extrusion of keratin using feathers, glycerol, and potassium sulphite mixture is one of them. Wrapping film can be produced using this method. Such film can be used for the production of packing materials and mulching sheets [3, 4].

Keratin is composed of 15.0-18.0% nitrogen, 1.5-2.0% phosphorus, and other nutritional elements so that the keratin-containing waste products (horn shavings, feather meal) are used for fertilization of plants [5, 6]. Since the aforementioned nutrients are incorporated into the organic compounds, they are not directly accessible to the plants. First, soil microorganisms have to decompose the complex organic molecules into mineral compounds. Mineral nitrogen release of osseous tissue takes longer than that of other products of animal origin. Fertilizers and soil improvement products made of osseous tissue can be used

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as slow release nitrogen fertilizers, improving nitrogen assimilation efficiency and decreasing the leaching of nitrogen into groundwater [7-11].

Waste products of animal origin can cause certain environmental problems when used as organic fertilizer. Nitrates, salts, and different infectious agents can easily contaminate surface water as well as groundwater. Manure and waste of animal origin can be used as an energy source in gas production or as a fuel [12, 13].

Lithuanian slaughter houses produce substantial amounts of cattle horn waste that needs to be utilized. Part of it is used in haberdashery production. Low-quality horns and the waste from haberdashery production are shredded and used for improvement of soil properties [14].

The aim of our study was to determine the chemical composition of cattle horn shavings produced in Lithuania, to conduct comparative experiments on the release of nitrogen compounds from cattle horn shavings and mineral fertilizers in water solutions and to determine the rate of mineralization of cattle horn shavings in soil.

Materials and Methods

The cattle horn shavings were obtained from the Algimantas Karkazas individual company, involved in production of haberdashery products. This company purchases the cattle horn waste products from UAB Utenos mėsa. Part of the horns is used in production of different commodity items, while another part goes to waste. This waste is shredded into shavings using a special mill. The performance of cattle horn shavings as fertilizer was compared to the multipurpose granular synthetic mineral fertilizer *Kemira* (NPK 14-11-25).

Determination of Chemical Composition of Cattle Horn Shavings

Dry matter content was determined by drying the samples at 105ºC, organic matter content was determined by combustion of the samples at 500ºC, organic carbon content was determined using the carbon analyzer TOC II, content of total nitrogen (N) was estimated using the Kjeldahl apparatus, ammonium nitrogen (NH_4–N) and nitrate nitrogen (NO_3–N) compounds were extracted in 20% HCl solution, and their concentrations were determined colorimetrically using FIAstar apparatus, pH_{KCl} was determined potentiometrically, total phosphorus (P) content was estimated colorimetrically using ammonium molybdate, total potassium (K) content was established using the flame emission spectrometry method, S content was determined turbodimetrically, Ca, Mg, Cr, Ni, Pb, Cu, and Zn content was measured using a flame atomizer (atomic absorption spectrometry), Cd content using an electrothermal atomizer (atomic absorption spectrometry), and Hg content was established using cold vapour atomic absorption spectrometry.

Determination of Granulometric Composition

100 g sample of horn shavings was passed through the set of Fritsch sieves (0.5, 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 mm). The share of each fraction was determined by weighing the horn shavings remaining on the sieve.

Estimation of Water Solubility of Nitrogen Compounds

1.0 g samples of horn shavings and synthetic mineral fertilizer were weighed, and then 100 ml of distilled water were added to each sample. The solutions were kept in a thermostat at 20±1ºC temperature. Concentrations of nitrates and ammonium nitrogen in these solutions were determined after 2, 24, 48, 96, and 144 hours. Concentration of nitrates was determined potentiometrically and concentration of ammonium nitrogen spectrometrically (LST ISO 7150-1).

Estimation of the Rate of Mineralization of Cattle Horn Shavings in Soil

Cattle horn shaving mineralization intensity was assessed by means of measuring the release of mineral nitrogen compounds from the shavings incorporated into soil during the growing period of organically grown winter wheat crop. The research on mineralization of horn shavings was conducted on the farm of organic production

Fig. 1. Cattle slaughter and horn waste production in UAB Utenos mėsa, 2008-12.

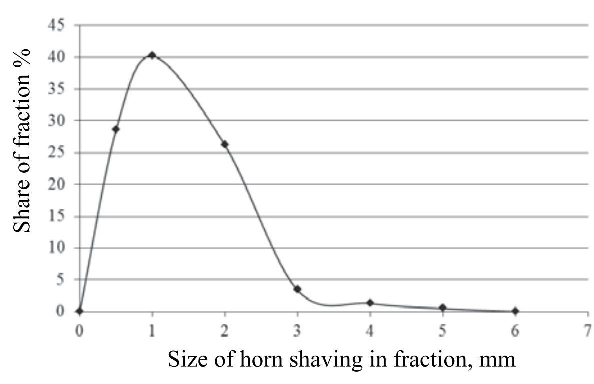

Fig. 2. Granulometric composition of horn shavings.

Table 1. Chemical composition of cattle horn shavings.

Constituent	Content
Dry matter	86.62±0.85 %
Organic matter	99.16±0.24 %
Organic carbon	39.97±0.43 %
Magnesium (Mg)	0.014±0.02 %
Total nitrogen (N)	15.54±0.35 %
Total phosphorus (P)	0.165±0.16 %
Total potassium (K)	0.09±0.02 %
Sulphur (S)	0.049±0.02 %
Calcium (Ca)	0.396±0.11 %
pH_{KCl}	7.2±0.1

at Aleksandras Sulginskis University, located in Kazliškės village, Kaunas region (54º52‘ N, 23º51‘ E). The soils of experimental field are *Endohypogleyi-Eutric Planosols – PLe-gln-w*.; according to the results of soil tests performed in 2008-09, the soil in experimental area was slightly alkaline (pH 7.2-7.4), medium-to-high in phosphorus (118-155 mg kg^{-1}), and medium in potassium (108-124 mg kg^{-1}); it had low-to-medium humus content (1.84-2.28%) and 0.109-0.122% of total nitrogen. In 2009-10 the soil was found to be slightly alkaline (pH 7.4), medium in phosphorus (134-147 mg kg^{-1}) and potassium (100-140 mg kg^{-1}), and with high humus content (3.17-3.34%), 0.184-0.213% of total nitrogen.

The soil samples for testing the agrochemical properties were collected from the experimental field using a soil auger. Samples were taken from 0-20 cm soil layer in 8-12 different spots, then the composite soil sample of 500 g was made. Three composite soil samples were collected in total and the sampling was conducted before the sowing of winter wheat. Soil pH_{KCl} was determined potentiometrically (ISO 10390) and the content of plant-available phosphorus and potassium was establishedd using the A–L method. Humus content was determined using dry combustion (ISO 10694), and total nitrogen content was estimated by Kjeldahl method.

Organically grown winter wheat crop was treated with cattle horn shavings before sowing at a rate of 30 kg N ha^{-1} (shavings were worked into the soil), and at tillering stage in spring at a rate of 50 kg N ha^{-1} (shavings were spread over the growing plants and not worked into the soil). The total size of a single experimental plot was 40 m^2 (4×10) and the netto size was 22 m^2 (2.2×10). The experiment was conducted in four repetitions. Winter wheat of Ada variety was sown after the oat-pea mixture grown for seed. Plant protection means were not used; potassium and phosphorus fertilizers were not applied.

Soil samples for determination of mineral nitrogen content in soil were taken using a soil auger from 0-30 cm soil layer in 5-8 different spots of the experimental plot. Soil samples were collected from all four repetitions. Soil sampling was conducted in autumn (before sowing), during the winter wheat tillering stage (BBCH 21), at the beginning (BBCH 31) and the end (BBCH 37) of stem elongation stage, and during the grain milk maturity stage (BBCH 73). Mineral nitrogen content in soil was determined spectrometrically.

The data obtained from our experiment was assessed using dispersion analysis method at the 95% accuracy level. Computer programme ANOVA [15] was used. Deviations were calculated from three experiments using the standard Excel program.

Weather conditions during our research varied substantially, and they had a significant effect on degradation of horn shavings as well as on the release of mine ral nitrogen compounds in soil. In 2008 the experimental plots were treated with cattle horn shavings on September 18. The total precipitation in 2008 was 176.3 mm (somewhat lower than multi-annual average), air temperature was higher than multi-annual average. In 2009 the field was fertilised on September 10. Precipitation in 2009 was 73.7 mm higher than in 2008, yet the air temperature was 0.6ºC lower. Mineral nitrogen content in soil was strongly affected by weather conditions in winter and in spring. During January, February, and March 2009 (before the soil sampling during the winter wheat tillering stage) total precipitation was 44.0 mm higher than that of the same period in 2010. An average air temperature was substantially higher. Cold weather in January and February of 2010 slowed down the mineralization of horn shavings in soil significantly. Mineral nitrogen content in soil was also affected by the precipitation and temperature levels in spring and summer. During the period from winter wheat tillering to full ripening in 2010 precipitation was 109.5 mm higher and air temperature 1.42ºC higher as compared to the same period of 2009. Weather conditions in 2010 were much more favourable for the degradation of horn shavings in soil than in 2009.

Results and Discussion

Cattle horn waste for production of horn shavings was obtained from UAB Utenos mėsa. In 2008-12 this company slaughtered 34,176-46,369 animals each year and produced 17,088-23,184 kg of cattle horn waste annually. This waste was used for the production of haberdashery items and soil improvement materials (i.e. horn shavings and horn core powder, Fig. 1.

The predominant (90%) size of horn shavings was within the range of 0.5-2.5 mm (Fig. 2). Granulometric

Table 2. Nitrogen-containing compounds in cattle horn shavings.

Nitrogen-containing compounds	Content
Ammonium nitrogen (NH_4-N)	540±147 mg kg^{-1}
Nitrate nitrogen (NO_3-N)	42±7 mg kg^{-1}
Mineral nitrogen incorporated in organic compounds	99.52%

Table 3. Contents of heavy metals in cattle horn shavings.

Element	Content
Chromium (Cr)	1.15±0.22 mg kg^{-1}
Cadmium (Cd)	0.003±0.001 mg kg^{-1}
Lead (Pb)	0.391±0.058 mg kg^{-1}
Copper (Cu)	6.68±0.49 mg kg^{-1}
Zinc (Zn)	118.0±8.0 mg kg^{-1}
Nickel (Ni)	-
Mercury (Hg)	-

composition of horn shavings was similar to that of mineral fertilizers.

The chemical composition of cattle horn shavings was determined. The horn shavings were found to consist of 86.62% dry matter, 99.16% organic matter, 39.97% organic carbon, 0.396% Ca, 0.165% P, 0.09% K, 0.049% S, and 0.014% Mg (Table 1). Horn shavings pH_{KCl} value was 7.2. Concentration of nitrogen (15.54%) was significantly higher than that of any other biogenic element. 99.52% of nitrogen was incorporated in slightly soluble organic compounds. Ammonium nitrogen (NH_4–N) constituted the major part of water soluble nitrogen compounds found in the horn shavings (Table 2).

From the chemical point of view cattle horn shavings could be regarded as nitrogen-rich organic fertilizer. As stated in the appropriate European Union legislative documents [16], horn shavings can be used in organic agriculture regardless of the way the cattle was raised. The data obtained from the Center of Agroecology at Aleksandras Stulginskis University suggests that cattle horn shavings can be used as an effective fertilizer for Gramineae family crops [14].

Horn shavings contained noticeable amounts of zinc (118.0 mg kg^{-1}) and copper (6.68 mg kg^{-1}). These elements might be useful for plants as micro-nutrients. Contents of other heavy metals in horn shavings were insignificant. Elements Hg and Ni were not found in the tested samples (Table 3).

The major part of heavy metals enters the animal body through food, and the lesser part is assimilated through water and air. Investigation of heavy metal levels in raw materials of animal origin used in manufacturing of food products for human consumption revealed that the number of samples with lead concentrations exceeding the maximum permissible level (4.7% of tested samples) was statistically significantly larger than that of the samples with exceedingly high cadmium concentrations (3.2% of tested samples). Liver of young cattle contained the highest levels of lead [17].

The concentrations of heavy metals in the tested cattle horn shavings are low. There is no threat of soil contamination through intensive use of horn shavings as fertilizer; copper and zinc are also microelements needed by plants.

Our research on release of water-soluble nitrogen compounds revealed that concentrations of ammonium

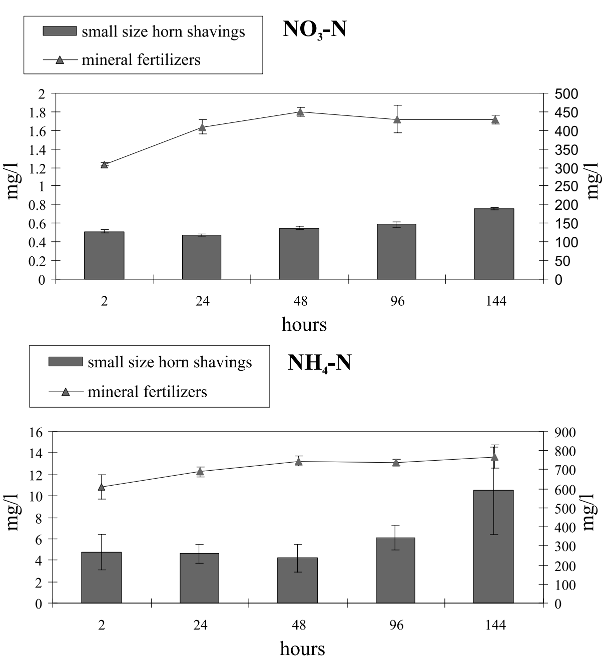

Fig. 3. Ammonium and nitrate nitrogen concentrations in solutions.

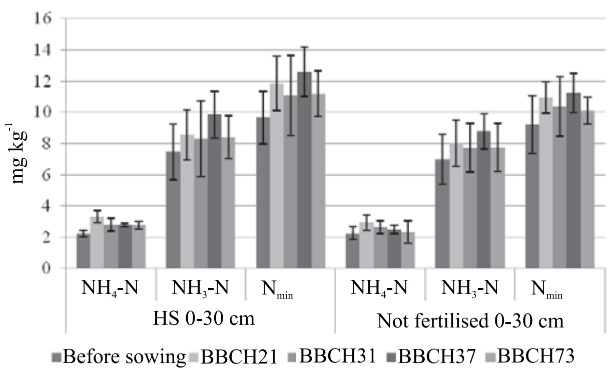

Fig. 4. Biodegradation of cattle horn shavings in soil at different development stages of organically grown winter wheat plants during the growing period of 2008-09.

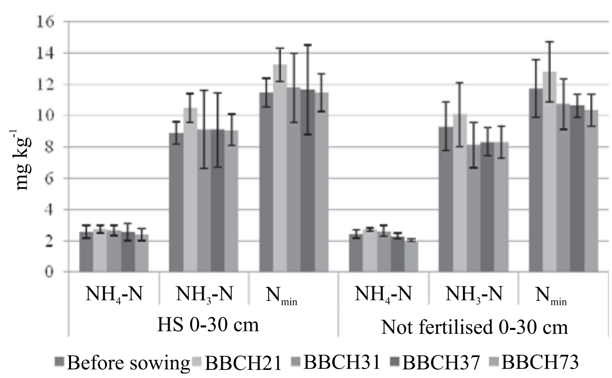

Fig. 5. Biodegradation of cattle horn shavings in soil at different development stages of organically grown winter wheat plants during the growing period of 2009-10.

nitrogen and nitrate nitrogen in mineral fertilizer solutions were 130 and 715 times, respectively, higher than those in cattle horn shavings solutions (Fig. 3). The ammonium and nitrate ratio was different. Ammonium nitrogen concentrations in solutions of cattle horn shavings and mineral fertilizer were 10.1 and 1.8 times, respectively, higher than nitrate nitrogen concentrations. Ammonium nitrogen concentration in cattle horn shaving solutions gradually increased from 5 to 11 mg l^{-1} in 6 days, yet still it was ca. 130 times lower than that in mineral fertilizer solutions. There were only traces of nitrate nitrogen found in cattle horn shaving solutions. Ammonium and nitrate nitrogen concentrations in mineral fertilizer solutions increased to the highest levels (700 and 400 mg l^{-1} respectively) in 2 days. Since the total nitrogen concentration in mineral fertilizer (14%) and cattle horn shavings (15,54 %) was almost the same, the obtained evidence suggests that nitrogen is released from mineral fertilizer hundreds of times faster than from cattle horn shavings. Plants cannot uptake the nitrogen as fast as it is released from mineral fertilizer, therefore part of nitrogen is leached into the deeper layers of soil and into the ground waters, resulting in environmental pollution. Cattle horn shavings are degraded by the soil microorganisms into simple mineral compounds first, thus the plants are getting the nutrients gradually.

Mineralization of cattle horn shavings started right after the incorporation of shavings into soil. In 2008-09, when winter wheat plants were in tillering stage (BBCH 21), the content of mineral nitrogen in 0-30 cm soil layer was 2.11 mg kg^{-1} higher than that determined before the sowing, while this difference in not fertilised plots was only 1.72 mg kg^{-1}. The numbers for 2009-10 growing period were 1.75 and 1.01 mg kg^{-1}, respectively. An increase of mineral nitrogen content in soil was not statistically significant – this result indicated that nitrogen compounds were released gradually; the speed of this release depended on weather conditions.

Low air temperature (yet still above zero) is typical for late autumn, winter, and spring; these conditions do not totally suppress the soil microorganisms, they only slow down their activity and the number of microorganisms decreases. Degradation of soil organic matter continues and mineral nitrogen compounds are released. Thus concentration of soil mineral nitrogen in spring is higher than in autumn. Activity of microorganisms intensifies as air temperature increases; organic matter is degraded more intensely and larger amounts of plant-available nitrogen compounds are released [18, 19].

Mineral nitrogen concentrations in soil treated with cattle horn shavings were higher than those in untreated soil at the beginning (BBCH 31) and the end (BBCH 37) of stem elongation stage and at the milk stage of kernel development (BBCH 73) during both growing periods. On the other hand, the only statistically significant difference (concentration of ammonium nitrogen by 0.35 mg kg^{-1} higher, $p < 0.05$) was obtained at the plant development stage BBCH 73 of 2010; the determined mineral nitrogen concentration increase was statistically insignificant in all other cases. Nitrogen compounds were released from the cattle horn shavings slowly, and part of them was taken up by winter wheat plants (Figs. 4 and 5).

The level of mineral nitrogen content in soil fluctuates in the course of the year. It depends on soil properties, cropping pattern, fertilizers applied, and weather conditions. Mineralisation and nitrification intensifies in spring due to the rising temperatures; this results in a sharp increase of mineral nitrogen concentrations in soil. The mineralization process activates when soil temperature reaches 10ºC, it is most intensive during the summer period, and the highest concentration of mineral nitrogen in soil is determined when soil temperature reaches 25-35ºC [20]. The rate of release of mineral nitrogen from organic compounds depends also on precipitation rates and air temperature. The process of mineral nitrogen release from organic compounds intensifies in spring; this intensification can also happen during the warm winter periods, causing the leaching of nitrogen compounds into groundwater [21-25].

Treatment of organically grown winter wheat crop with cattle horn shavings resulted in the slow release of mineral nitrogen; plants were able to take it up at the right time. Higher concentrations of mineral nitrogen in soil result in higher yields of winter wheat [26]. Since the mineral nitrogen is released from cattle horn shavings gradually, the shavings can be considered as long-lasting soil-improving organic material.

Conclusions

1. Cattle horn shavings obtained from cattle horn waste contained significant amounts of total nitrogen (>15%), 99% of which were in organic form and only very small amounts in ammonia and nitrate forms. Concentration of ammonia nitrogen was more than 12 times higher than the concentration of nitrate nitrogen. In addition, the horn shavings were found to contain certain amounts of phosphorus and potassium. Contents of different heavy metals in horn shavings were insignificant: micro amounts of zinc and copper were found, and only traces of chrome and lead were determined.
2. Our research on the release of water-soluble nitrogen compounds from the cattle horn shavings in comparison to mineral fertilizers revealed that the concentration of ammonia nitrogen increased gradually and reached the level of 11 mg/l concentration in 6 days, which was 130 times less compared to the concentration of ammonia nitrogen released by the mineral fertilizers. Only the traces of nitrate nitrogen were detected in the water solution of cattle horn shavings – 715 times less compared to the water solution of the mineral fertilizers.
3. Research conducted on the effect of cattle horn shavings on agrochemical soil properties revealed that cattle horn shavings can be regarded as an ecological long-lasting nitrogen-rich organic fertilizer. It releases the nitrogen slowly, therefore the concentration of mineral nitrogen content in soil increases gradually.

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