

EFFECT OF ASH-FLY ASH MIXTURE APPLICATION ON SOIL FERTILITY*

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Abstract

Nowadays, it is illegal to apply ashes, fly ashes and their mixtures on arable soil in Slovakia although it is allowed in many countries. The reasons why the Slovak law prohibits using these substances in agriculture are not explicitly stated but most probably it is so because of the variable and often high content of heavy metals as well as the residual radioactivity in soil treated with such mixtures. However, ashes and fly ashes are significantly different in parameters, therefore they should be classified individually. It is irrational to ignore some positive effects of ashes and fly ashes on plants if they do not pose a threat of increased input of heavy metals and residual radioactivity into soil and, subsequently, in crops. The aim of this experiment has been to find out the effect of ash-fly ash mixture (AFAM) on some soil yielding parameters and to clarify opinions on using ashes and fly ashes in agriculture.

A pot experiment was carried out in a vegetation cage located in the premises of the SAU in Nitra. Pots of the capacity of 30 kilos were filled with 24 kg of anthropogenic soil prepared by mixing two portions of Haplic Luvisol with one portion of siliceous sand. The ash-fly ash and/or NPK fertilizers were applied into the whole soil profile. The experimental design comprised 6 treatments (0, AFAM₁, NPK, NPK+ AFAM₁, NPK+ AFAM₂, NPK+ AFAM₃), each in four replications, as follows: 1 – control treatment, 2 – AFAM in a dose of 3 t ha⁻¹, 3 – NPK mineral fertilizer, 4 – NPK mineral fertilizer + AFAM in a dose of 3 t ha⁻¹, 5 – NPK mineral fertilizer + AFAM in a dose of 30 t ha⁻¹, 6 – NPK mineral fertilizer + AFAM in a dose of 150 t ha⁻¹. The soil samples were analysed in the whole soil profile after harvest of spring barley.

The ash-fly ash mixture in the basic dose of 3 t ha⁻¹ positively influenced several soil parameters. Statistically significant increase of both pH_{KCl} and pH_{H₂O} as well as the con-

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tent of available calcium were noted. The total carbon content (C_{ox}), carbon of humic substances (C_{HS}), carbon of humic acids (C_{HA}), carbon of fulvic acids (C_{FA}) and available K also increased but not significantly. Sorption capacity (CEC) did not change. The sum of exchangeable base cations (EBC), base saturation (BS), conductivity (EC) and content of N_{in} and Mg were not significantly influenced. The AFAM with NPK combination significantly decreased the bulk density of soil (BD). Addition of AFAM to mineral NPK fertilizers at the rates of 3, 30 and 150 t ha⁻¹, respectively, influenced positively the content of C_{ox} , C_{HS} , C_{HA} , Mg and the values of CEC, EBC, BS, BD, pH_{H_2O} and pH_{KCl} . This addition had a negative effect on just two parameters: EC and content of mineral nitrogen. Application of ash-fly ash mixture alone or with NPK fertilizers improved soil parameters, which enhanced the soil productivity and its resistance against depressed fertility caused by unidirectional industrial nutrition.

Key words: ash-fly ash mixture, soil fertility, total carbon, humic acids, bulk density of soil.

WPLYW STOSOWANIA POPIOŁÓW, POPIOŁÓW LOTNYCH I ICH MIESZANEK NA ŻYZNOŚĆ GLEBY

Abstrakt

Aplikacja popiołów, popiołów lotnych i ich mieszanek w glebach Słowacji nie jest dozwolona przez prawo, mimo że niektóre państwa pozwalają na takie wykorzystanie. Można przypuszczać, że jest to spowodowane głównie niestabilną i często wysoką zawartością metali ciężkich oraz związków promieniotwórczych w glebie. Poszczególne popioły i popioły lotne znacznie różnią się powyższymi parametrami, z tego powodu konieczna jest indywidualna ocena wykorzystania popiołów w Słowacji. Korzystnego wpływu popiołów i popiołów lotnych na rośliny nie można pominąć w przypadku surowców nie stwarzających zagrożenia związanego ze zwiększoną ilością metali ciężkich i związków radioaktywnych. Celem eksperymentu było określenie wpływu mieszanki popiołu z popiołem lotnym (AFAM) na niektóre parametry glebowe oraz sprecyzowanie poglądów na wykorzystanie popiołów i popiołów lotnych w rolnictwie.

Eksperyment przeprowadzono w vegetacyjnej klatce znajdującej się na terenie Słowackiego Uniwersytetu Rolniczego w Nitrze, w 30 kg pojemnikach z 24 kg antropogenicznej gleby, która powstała po zmieszaniu 2 części brunatno-modalnej gleby i 1 części piasku krzemionkowego. Do całego profilu glebowego powyższych pojemników aplikowano mieszankę popiołów i popiołów lotnych lub nawozów NPK w 4 powtórzeniach. Eksperyment miał 6 wariantów (0, AFAM₁, NPK, NPK+ AFAM₁, NPK+ AFAM₂, NPK+ AFAM₃): 1 – wariant kontrolny, 2 – mieszanka popiołu i popiołu lotnego w ilości 3 t ha⁻¹, 3 – nawozy sztuczne NPK, 4 – nawozy NPK + AFAM w ilości 3 t ha⁻¹, 5 – nawozy NPK + AFAM w ilości 30 t ha⁻¹, 6 – nawozy NPK + AFAM w ilości 150 t ha⁻¹.

Mieszanka popiołu i popiołu lotnego (AFAM) stosowana w ilości 3 t ha⁻¹ miała pozytywny wpływ na kilka parametrów glebowych. Istotnie statystycznie zwiększyła wartość pH_{KCl} , pH_{H_2O} i dostępnych zasobów Ca. W przypadku zawartości węgla całkowitego (C_{ox}), węgla substancji humusowych (C_{HS}), węgla kwasów huminowych (C_{HA}), kwasów fulwia (C_{FA}) i dostępnego K reakcja na wzrost była niejednoznaczna. Gęstość objętościowa gleby (BD) się zmniejszyła. Absorpcja (CEC) nie uległa zmianie. Statystycznie nieistotny, ale negatywny wpływ miała na ilość kationów podstawowych (EBC), stopień nasycenia kationami bazowymi (BS), przewodność (EC), zawartość N_{an} i Mg.

Dodanie AFAM do nawozów NPK w dawkach 3, 30 i 150 t ha⁻¹ miało pozytywny wpływ na ilości C_{ox} , C_{HS} , C_{HA} i Mg, na wartości CEC, EBC, BS, pH_{KCl} i pH_{H_2O} , BD gleby. Negatywnie wpłynęło tylko na EC i zawartość N_{in} . Wykorzystanie mieszanki popiołu i popiołów lotnych oraz mieszanki w połączeniu z nawozami NPK poprawiło głównie te pa-

rametry gleby, które zwiększają jej wydajność, odporność na spadek plonów spowodowany jednostronnym sztucznym nawożeniem roślin.

Słowa kluczowe: mieszanka popiołów i popiołów lotnych, żyzność gleby, węgiel całkowity, kwasy huminowe, gęstość gleby.

INTRODUCTION

Thermal power stations produce approximately 500 million tons of ash and 100 million tons of fly ash annually all over the world. About 15-20% of ash and about 20-40% of fly ash are recycled (WRIGHT et al. 1998, KIKUCHI 1999). In Slovakia, however, only about 10-15% of ash and fly ash are used again and with their annual production of about 1.1-1.2 million tons it means a growing pressure for new storage space, which should be used more appropriately and ecologically. Therefore, Slovak researchers are looking for possibilities of using ashes, fly ashes and their mixtures in the building industry, mining and metallurgical industry and automobile industry (FLOREKOVÁ et al. 2001). It seems that agriculture could be another possible recipient of these substances but the Slovak law does not allow it. The negative approach to ashes, fly ashes and their mixture in Slovakia remains in contrast to the substantial international experience of using these substances in agriculture (AMRHEIN et al. 1995, LIN et al. 1998, KIKUCHI 1999, MATSI, KERAMIDAS 1999, JALA, GOYAL 2006, JEZIEWSKA-TYS, FRAC 2008, ANTONKIEWICZ 2010). The cause of negative attitudes to using ashes and fly ashes in Slovakia has never been explicitly stated but apparently it is so due to their unstable nature, frequently high content of heavy metals, high salinity and reduction of solubility of some nutrients by their high pH values as well as the residual radioactivity (AITKEN et al. 1984, KARANGELOS et al. 2004, BASU et al. 2009). It is therefore inevitable to classify specific ashes and fly ashes individually in Slovakia, on the basis of exactly defined chemical and radiological criteria (parameters) and agrochemical and environmental influence on soil and plants. It is wrong to ignore considerable qualitative differences among particular ashes and fly ashes with respect to their positive influence on crops and soil.

The aim of this experiment has been to find out the effect of AFAM (in which the content of heavy metals and also residual radioactivity were lower than the limits set by the Slovak law, KOVÁČIK, MIŠÍK 2008) on the soil yielding parameters, and to clarify opinions on using ashes and fly ashes in agriculture.

MATERIAL AND METHODS

A pot experiment was carried out in 2005 and 2006 in a vegetation cage located in the premises of the SAU in Nitra (48°18' N, 18°05' E). The experimental pots were filled with a mixture of 16 kg of soil (Haplic Luvisol) and 8 kg of siliceous sand; the agrochemical characteristics of the soil material are presented in Table 1. The chemical parameters of N-NH₄ were determined by Nessler's colorimetric method; N-NO₃ was assayed by the colorimetric method with phenol – 2,4 disulphonic acid and N_{in} was calculated as the sum N-NH₄ + N-NO₃. The content of available P, K, Ca and Mg was determined by Mehlich III extraction procedure (MEHLICH 1984). The content of P was determined by the colorimetric method while K and Ca were measured by flame photometry; the content of Mg was assessed by atomic absorption spectrophotometry and pH_{H2O} and pH_{KCl} (in solution of 1.0 mol KCl dm⁻³) were determined potentiometrically. The total N content (N_t) was determined according to Kjeldahl's method (BREMNER 1960); total carbon content (C_{ox}) was evaluated spectrophotometrically after oxidation (TJURIN 1966); exchangeable base cations (EBC), cation exchange capacity (CEC) and base of saturation (BS) were tested according to Kappen's method (MYŚLIŃSKA 1998). Soil electrical conductivity (EC) was also determined (CORWIN, LESCH 2005).

The hygienic, toxicological and agrochemical parameters of the material are presented in Tables 2 and 3. The detected metal content was lower than the permitted limits for soil additives used in arable soil. The total forms of metals in the soil were determined by the means of an AAS Pye Unicam (mineralization in HF + HClO₄).

In the ash-fly ash mixture applied, the presence of radioactive substances was analyzed by semiconductor gamma-spectrometry using a high purity germanium detector (Canberra). The whole assembly of a detector, modular spectrometer (EG&G Ortec, Canberra) and software (GammaVision + modified modules of Nuclear Data software) passed relevant comparison tests organized by the International Atomic Energy Agency. No activity (MDA < 0.29 Bq kg⁻¹) of environmentally important man-made radionuclides (¹³⁷Cs, ¹³⁴Cs, ⁶⁰Co) was found in the ash-fly ash substrate. The levels of natural U and Ra in ash-fly ash mixture exceeded the levels in soil by a factor ≤ 2.0, but were more than 4.1-fold lower than the most active natural isotope ⁴⁰K found (382 ± 31) Bq kg⁻¹. Those levels of radioactivity are well in the range of the usual variability of natural isotopes in soils (MAZZILLI et al. 2000) and therefore no build-up of radioactivity in soil and plants could be produced by introducing the ash-fly ash mixture to soil at the suggested application rate.

Into each pot, 100 spring barley grains (Express c.v.) was seeded. After germination, the seedlings was thinned to 75 plants per pot. Moisture of the soil in the pots was maintained at 60% of full water capacity by regular irrigation.

Table 1

Agrochemical characteristics of anthropogenic soil used in pot trial

Year	N-NH ₄	N-NO ₃	Ni _n	P	K	Ca	Mg	N _t	C _{ox} (%)	CEC		BS (%)	pH _{KCl}	EC (mS cm ⁻¹)
										EBC (mmol kg ⁻¹)	CEC (mmol kg ⁻¹)			
2005	12.48	0.24	12.72	41.3	242	1 310	250	1064	0.97	87.8	101.5	86.5	5.78	0.040
2006	9.80	2.99	12.80	18.9	182	1 643	303	1064	0.99	90.6	106.4	85.1	5.57	0.025

Table 2

The heavy metals content in ash-fly ash mixture used in the pot trial

As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
< 0.04	< 1	34.0	34.3	28	7 025	0.366	960	27	< 5	26.8
10.0*	2.0*	-	100.0*	-	-	1.0*	-	50.0*	50.0*	-

*Limited values of heavy metals for soil additives (according to Slovak Law Act No 577/2005).

Table 3

Agrochemical characteristics of ash-fly ash mixture used in the pot trial

N-NO ₃	N-NH ₄	N _{in}	P	K	Ca	Mg	pH _{KCl}	pH _{H₂O}	EC (mS cm ⁻¹)	CaCO ₃ (%)	C _{ox} (%)
1.1	2.6	3.7	12	109	3400	1450	12.35	12.12	0.05	1.51	4.43

The experiment consisted of 6 treatments (0, AFAM₁, NPK, NPK+ AFAM₁, NPK+ AFAM₂, NPK+ AFAM₃). Each treatment was conducted in four replications. The basic rate of ash-fly ash mixture (AFAM₁) was applied in treatments 2 and 4 and represented 0.1% of the total weight of soil in a pot (24 g pot⁻¹, i.e. 3 t ha⁻¹). The rate of ash-fly ash mixture applied in treatment 5 (AFAM₂) was 10-fold (240 g pot⁻¹, that is 30 t ha⁻¹) and in treatment 6 (AFAM₃) 50-fold (1200 g pot⁻¹, that is 150 t ha⁻¹) higher than the basic rate.

The rates of NPK nutrients were calculated on the basis of the content of N_{in} and available P and K in soil and the plant requirement for these nutrients to achieve planned yield. Nitrogen was applied in the form of DAM-390 fertilizer; P was added in the form of single superphosphate and potassium was introduced to soil as 60% KCl.

Spring barley was harvested at the growth stage of DC 91. After harvest, a soil sample of the whole profile from the each pot was taken and the following parameters were determined: C_{ox} – total carbon, C_{HS} – carbon of humic substances, C_{HA} – carbon of humic acids, C_{FA} – carbon of fulvic acids, soil reaction – pH_{KCl}, BD – bulk density. The parameters C_{HS}, C_{HA} and C_{FA} were detected according to the methods described by KONONOVA and BELTCHIKOVA (SHVIDENKO et al. 1997). The results were evaluated by analysis of variance, using Statgraphics, version 5 software.

RESULTS AND DISCUSSION

Application of ash-fly ash mixture (AFAM, treatment 2) at the rate of 3 t ha⁻¹ positively influenced several pedological and agrochemical soil characteristics (Tables 4 and 5). The application caused statistically significant increase of both pH_{KCl} and pH_{H₂O} as well as the content of available calcium. Owing to this attribute, KOVÁČIK and SLAMKA (2008) recommend to use shes and fly ashes for adjustment of pH in acid soils. The only exception is acid ashes, which lost their alkaline elements in the process of weathering and leaching (DOSSKEY, ADRIANO 1993).

After application of AFAM, the content of total carbon (C_{ox}), carbon of humic substances (C_{HS}), carbon of humic acids (C_{HA}), carbon of fulvic acids (C_{FA}) and available K increased. However, this increase was not statistically significant. On the other hand, significant increase of carbon content was reported by CERVELLI et al. (1987) and SAJWAN et al. (2003).

After AFAM application, the soil bulk density (BD) decreased, which agrees with the findings of PERKINS and VANN (1997) but is in contrast to the report by CHANG et al. (1977). Sorption capacity (SC) was nearly unchanged.

The base saturation (BS), exchangeable base cations (EBC), conductivity (EC) and content of N_{in} and Mg were negatively affected, but the influence was negligible and statistically insignificant (Tables 4, 5).

Table 4

The effect of ash fly-ash mixture on some agrochemical parameters

Treatment		pH _{KCl}	pH _{H₂O}	EC	Nin	P	K	Ca	Mg
No.	designation			(mS cm ⁻¹)	(mg kg ⁻¹)				
1	0	5.63 ^a	6.80 ^a	0.06 ^a	12.55 ^a	52.5 ^b	210 ^{ab}	900 ^a	262 ^{ab}
2	AFAM ₁	5.93 ^b	7.00 ^b	0.07 ^a	11.15 ^a	32.2 ^a	220 ^b	1 401 ^c	253 ^a
3	NPK	5.60 ^a	6.71 ^a	0.14 ^b	38.83 ^d	61.5 ^{bc}	200 ^a	1 310 ^c	241 ^a
4	NPK+AFAM ₁	5.92 ^b	6.81 ^a	0.14 ^b	34.48 ^c	57.6 ^{bc}	200 ^a	1 173 ^b	241 ^a
5	NPK+AFAM ₂	6.25 ^c	7.08 ^b	0.17 ^c	27.48 ^b	65.7 ^c	218 ^{ab}	1 401 ^c	292 ^b
6	NPK+AFAM ₃	6.90 ^d	7.40 ^c	0.24 ^d	25.39 ^b	91.3 ^d	255 ^c	1 538 ^d	443 ^c
LSD _{0.05}		0.271	0.103	0.025	3.503	10.85	20.0	101.6	38.5
LSD _{0.01}		0.366	0.139	0.033	6.365	14.58	26.9	139.7	46.5

LSD – limit of significant difference at the level = 0.05 and = 0.01.

The degree of soil salinity and deterioration of the BS and EBC parameters were considerably lower after an application of 3 t ha⁻¹ AFAM than after a standard rate of mineral NPK fertilizers. Application of NPK fertilizers (treat.3) deteriorated most of the examined pedological and agrochemical parameters (C_{ox} , C_{HS} , C_{HA} , C_{FA} , ratio of $C_{HA}:C_{FA}$, CEC, EBC, BS, pH_{KCl}, pH_{H₂O}, EC) not only in comparison with the unfertilized treatment 1, but also with treatment 2 (AFAM₁). In contrast, addition of AFAM at the rates of 3, 30 and 150 t ha⁻¹, respectively to mineral NPK fertilizers (treatments 4, 5, 6 versus treatment 3) not only mitigated the demonstrated negative effect of NPK fertilizers on the majority of the parameters, but many affected positively (C_{ox} , C_{HS} , C_{HA} , ratio of $C_{HA}:C_{HF}$, CEC, EBC, BS, pH_{H₂O}, pH_{KCl}, BD). The gradually increasing rates of AFAM added to NPK fertilizers increased the values of the above parameters, except soil bulk density, which decreased with the increasing rates of AFAM, but this was considered as a positive development (Table 5).

When 150 t ha⁻¹ of AFAM was applied (treatment 6), the ratio of $C_{HA}:C_{FA}$ was lowered and the conductivity increased significantly. From this viewpoint, this rate could be considered risky but only if such rates of AFAM are applied in short time intervals. The recorded conductivity of 0.24 mS cm⁻¹ (treatment 6) was much below 2 mS cm⁻¹, which classifies soil as slightly salinated. Increased EC values after application of fly-ash rates over 40 t ha⁻¹ are cited by several authors (CLARK et al. 1999, MATSI, KERAMIDAS 1999). Our findings prove that it is unreasonable to perceive the AFAM rate used in the experiment as “material hazardously increasing the content of salts in soil”.

Table 5

The effect of ash fly-ash mixture on some pedological parameters

No.	Treatment designation	Cox	CHS	CHA		CFA	C : N	C _{HA} : C _{FA}	CEC	EBC	BS	BD
				Cox								
1	0	0.954 ^a	0.369 ^a	0.164 ^{ab}	0.205 ^a	12.4	0.800	120.3 ^{ab}	109.6 ^a	91.16	1.40 ^b	
2	AFAM ₁	1.099 ^a	0.392 ^a	0.170 ^{bc}	0.222 ^a	14.1	0.766	119.8 ^{ab}	107.1 ^a	89.42	1.31 ^{ab}	
3	NPK	0.893 ^a	0.333 ^a	0.137 ^a	0.196 ^a	11.4	0.699	115.0 ^a	104.0 ^a	90.43	1.34 ^{ab}	
4	NPK+AFAM ₁	1.106 ^a	0.368 ^a	0.185 ^{cd}	0.183 ^a	14.5	1.011	117.0 ^{ab}	105.8 ^a	90.44	1.28 ^a	
5	NPK+AFAM ₂	1.348 ^a	0.419 ^a	0.209 ^d	0.210 ^a	15.7	0.995	128.7 ^{ab}	119.4 ^{ab}	92.80	1.26 ^a	
6	NPK+AFAM ₃	2.057 ^b	0.716 ^b	0.210 ^d	0.506 ^b	37.7	0.415	141.2 ^b	137.0 ^b	96.98	1.23 ^a	
LSD _{0.05}		0.596	0.160	0.026	0.077			24.28	24.64		0.117	
LSD _{0.01}		0.805	0.216	0.035	0.105			32.78	33.27		0.158	

LSD – limit of significant difference at the level = 0.05 and = 0.01.

The C:N ratios fluctuated in the range from 11.4:1 to 37.7:1 in individual treatments. The lowest value of the ratio was calculated in the treatment with NPK fertilizers application, which is in accordance with the findings of KOVÁČIK and WISNIEWSKA-KIELIAN (2009), who stated that mineral fertilizers intensify the mineralization process, causing a decline in the carbon content in soil on but increasing the content of available nutrients. This effect of mineral fertilizers is evaluated positively by farmers. However, in the long run, intense mineralization of organic matter is negative for its maintenance in the soil (ŠIMANSKÝ et al. 2008).

The latest findings by RASOOL et al. (2008) indicate that soils poor in organic matter, when treated with mineral fertilizers in proper rates, may be enriched in carbon released through more roots growing in that soil.

The highest C:N ratio was found in treatment 6, where – beside the application of mineral fertilizers that lowered the C:N ratio – AFAM at a rate of 150 t ha⁻¹ was added. This indirectly confirms that ashes produce an inhibitory effect on microflora involved in the mineralization processes.

Application of AFAM in all the treatments and combinations (treatment 2 versus 1 and treatments 4, 5, 6 versus 3) caused reduction of the N_{in} level in soil. Increasing rates of AFAM proportionally decreased the N_{in} content in soil (Table 4). These findings verify the hypothesis on possible inhibition caused of AFAM on the mineralization microflora. Nearly the same conclusions were reached by PATHAN et al. (2002).

CONCLUSIONS

The results show that AFAM applied 2 weeks before barley sowing at the rate of 3 t ha⁻¹ positively influenced several soil parameters. The values of pH_{KCl}, pH_{H₂O} and the content of available Ca were significantly increased. The content of total carbon (C_{ox}), carbon of humic substances (C_{HS}), carbon of humic acids (C_{HA}), carbon of fulvic acids (C_{FA}) and available K also increased but not significantly. The soil bulk density (BD) decreased and the cation exchange capacity (CEC) showed no change. The following characteristics were not significantly influenced: exchangeable base cations (EBC), base saturation (BS), conductivity (EC) and the content of N_{in} and Mg.

Application of AFAM in all the treatments and combinations caused reduction of the N_{in} level in soil and N_{in} content decreased proportionally with the increasing rates of AFAM.

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