

EFFECT OF LIMING AND MINERAL FERTILIZATION ON CADMIUM CONTENT IN GRAIN OF SPRING BARLEY (*HORDEUM VULGARE* L.) AND WINTER WHEAT (*TRITICUM AESTIVUM* L.) CULTIVATED ON LOESSIAL SOIL

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Abstract

In 1986-2001, a two-factor, strict experiment was conducted on a field subjected to static fertilization, situated in the Rzeszów Foothills (Pogórze Rzeszowskie, S-E Poland). The experiment was set up in a random sub-block design with 4 replications. The first variable was liming (A) and the second one consisted of different mineral fertilization variants (B). The basic level of fertilization ($N_1 P_1 K_1$) was 80 kg N ha⁻¹, 100 kg P₂O₅ ha⁻¹ and 120 kg K₂O ha⁻¹ under spring barley and 90 kg N ha⁻¹, 80 kg P₂O₅ ha⁻¹, 100 kg K₂O ha⁻¹ under winter wheat. Liming did not prove to have any significant effect on the cadmium content in spring barley and winter wheat grain, although the latter tended to decline in response to the treatment.

Mineral NPK fertilization, applied in higher doses, significantly raised the content of cadmium, especially in spring barley grain, but less in winter wheat grain. No statistical correlation was proven between the influence of liming and mineral fertilization on the cadmium content in grain of the two cereals. However, the cadmium content was generally lower in grain of cereals cultivated on fertilized objects where liming was applied.

Key words: cadmium, liming, mineral fertilization, spring barley, winter wheat.

**WPLYW WAPNOWANIA I NAWOŻENIA MINERALNEGO NA ZAWARTOŚĆ KADMU
W ZIARNIE JĘCZMIENIA JAREGO (*HORDEUM VULGARE* L.) I PSZENICY OZIMEJ
(*TRITICUM AESTIVUM* L.) UPRAWIANYCH NA GLEBIE LESSOWEJ**

Abstrakt

W latach 1986-2001 przeprowadzono dwuczynnikowe statyczne doświadczenie polowe zlokalizowane na Podgórzu Rzeszowskim (południowo-wschodnia Polska). Doświadczenie dwuczynnikowe w 4 powtórzeniach założono metodą bloków losowanych z podblokami. Pierwszym czynnikiem było wapnowanie (A), drugim – niezależne od wapnowania zróżnicowane nawożenie mineralne (B). Podstawowy poziom nawożenia ($N_1P_1K_1$) dla jęczmienia jarego wynosił: 80 kg N ha⁻¹, 100 kg P₂O₅ ha⁻¹ i 120 kg K₂O ha⁻¹, natomiast dla pszenicy ozimej: 90 kg N ha⁻¹, 80 kg P₂O₅ ha⁻¹, 100 kg K₂O ha⁻¹. Nie udowodniono istotnego wpływu wapnowania na zawartość kadmu w ziarnie jęczmienia jarego i pszenicy ozimej, jednakże zaobserwowano tendencję do zmniejszania się zawartości kadmu w ziarnie zbóż pod wpływem wapnowania.

Nawożenie mineralne NPK stosowane w wysokich dawkach miało istotny wpływ na wzrost zawartości kadmu, szczególnie w ziarnie jęczmienia jarego, w mniejszym stopniu w ziarnie pszenicy ozimej. Nie stwierdzono istotnych statystycznie interakcji wapnowania i nawożenia mineralnego w kształtowaniu się zawartości kadmu w ziarnie badanych zbóż, jakkolwiek zawartość kadmu była generalnie niższa w ziarnie zbóż uprawianych w obiektach nawozowych z zastosowaniem wapnowania.

Słowa kluczowe: kadm, wapnowanie, nawożenie mineralne, jęczmień jary, pszenica ozima.

INTRODUCTION

Accumulation of cadmium in soils and plants is determined by the sub-soil geological type (GORLACH 1995, KANIUCZAK, HAJDUK 1995, GORLACH, GAMBUŚ 1996, KANIUCZAK, HAJDUK 2000, LIPIŃSKI 2000), as well as any use of waste for fertilization (MERCİK et al. 1997, KOĆAŃ et al. 2008) and intensive phosphorus fertilization (GORLACH, GAMBUŚ 1997, KANIUCZAK, HAJDUK 2000). Besides, atmospheric emissions caused by natural processes and human activities add their share of cadmium. Industry, including power industry, and transportation are among more significant sources of trace elements emitted to the atmosphere (PACYNA, PACYNA 2001, FRIESL-HANL et al. 2009).

Cadmium is extremely readily taken up by plants, both by their roots and leaves, usually in proportion to the cadmium content in the environment. Contamination of soil with cadmium may reduce the mass of aerial parts and vary the concentration of macronutrients in plants (WYSZKOWSKI, WYSZKOWSKA 2009). Cadmium is assimilated by plants independently from soil properties. Such good phyto-assimilation of cadmium poses a risk of its direct intake in excessive quantities. Cereal grains are a potential threat, too, because bakery and flour products constitute approx. 20% of human diet. Cadmium accumulation in wheat grain is positively correlated with the quantity of silt and with its content in soil (LIPIŃSKI 2000), but is negatively affected by the soil pH value and sorptive capacity (WŁAŚNIEWSKI 2000). Much

research has dealt with the cadmium concentration in grain of cereals (wheat, rye, barley, oats) cultivated on soils with natural content of this element. Wherever the soil lay in a zone affected by refineries and oil-industry, the cadmium content in harvested grain exceeded acceptable levels for edible plants (INDEKA, KARACZUN 2000). The results of this research indicate another source of cadmium in cereal grain, i.e. atmospheric precipitation. It is very important for human health to reduce cadmium in cereal grain. Cadmium in wheat grain can be limited by soil liming (OLIVER et al. 1996). Liming and manure fertilization also lower the cadmium content in wheat and spring barley grain (SINGH et al. 1989). In addition, liming and mineral NPK Mg fertilization restrict the phyto-assimilation of cadmium (KANIUCZAK 1997). Cadmium solubility is controlled by soil pH (JANSSON 2002).

The purpose of this research has been to determine the effect of agrochemical treatments (liming and mineral fertilization) on the behavior of cadmium in grain of spring barley (*Hordeum vulgare* L.) and winter wheat (*Triticum aestivum* L.).

MATERIAL AND METHODS

In 1986-2001, a two-factor, strict experiment was conducted on a field subjected to static fertilization, situated in the Rzeszów Foothills (Podgórze Rzeszowskie). The experiment was set up in a random sub-block design with 4 replications. The area of each plot (fertilization treatment) was 30 m². The first variable was liming (A) and the second consisted of different mineral fertilization variants (B), independent from liming. In this experiment, the first sub-block was left without liming (A₁) and the second one was limed (A₂). The following crops were cultivated in a four-year crop rotation cycle: potato, spring barley, fodder sunflower, (fodder cabbage in the 1st crop rotation cycle) and winter wheat. The study covered 4 crop rotation cycles. Spring barley was grown in 1989, 1993, 1997 and 2001, whereas winter wheat was cultivated in 1987, 1991, 1995 and in 1999. The soil on which the experiments were set up was formed from loess of grey-brown podzolic type (Haplic luvisols), of the grain-size distribution of fine silt, and was characterized by high acidification in the Ap arable humus layer and Bt enrichment layer. The total content of trace elements (Cu, Zn, Ni, Co, Cd, Pb) in the soil was on the natural level and did not differ from their content in loess soils in other regions of Poland.

The mean content of cadmium in the mineral fertilizers applied in this experiment ranged from 0.03 mg Cd kg⁻¹ in magnesium sulfate, through 0.36 mg Cd kg⁻¹ in limestone oxide fertilizer, to 5.36 mg Cd kg⁻¹ in triple superphosphate.

Liming was applied every 4 years (in a dose calculated per 1Hh), prior to sowing a consecutive crop in the rotation. Different mineral NPK fertilization covered 14 fertilized plots in each sub-block. The basic level of fertilization ($N_1 P_1 K_1$) was 80 kg N ha⁻¹, 100 kg P₂O₅ ha⁻¹ and 120 kg K₂O ha⁻¹ under spring barley and 90 kg N ha⁻¹, 80 kg P₂O₅ ha⁻¹, 100 kg K₂O ha⁻¹ under winter wheat. Potatoes, spring barley and winter wheat were fertilized with magnesium in a dose of 40 kg MgO ha⁻¹; the magnesium dose for fodder sunflower was 120 kg MgO ha⁻¹ (in crop rotations 1986-1989 and 1990-1993), but was reduced to 40 kg MgO ha⁻¹ in the two subsequent crop rotations (1994-1997 and 1998-2001). Grain samples were dried at 105°C and mineralized in a mixture of concentrated acids (HNO₃ : HClO₄ : H₂SO₄) in 20:5:1 proportions, using a Tecator digestion system DS 40. The cadmium content was determined using flame spectrophotometry (FAAS), after APDC complexing and extraction of the formed complex to the organic phase of methyl-isobutyl ketone (MIBK). The data were statistically processed using two-factor analysis of variance and calculating the lowest significant difference (LSD) with Tukey's test at significance levels $p=0.05$ and $p=0.01$.

RESULTS AND DISCUSSION

The mean content of cadmium in spring barley and winter wheat grain varied largely depending on liming (A) and mineral fertilization (B) – Tables 1, 2. Cadmium in grain of barley and wheat cultivated on unlimed soil varied within a wider range compared to the cereals grown on limed soil. The maximum threshold level for cadmium in edible plants, as set by the Polish Institute of Soil Science and Plant Cultivation (IUNG) (i.e. not higher than 0.15 mg kg⁻¹ of dry matter), was exceeded in the grain of barley fertilized with the double dose of NPK fertilizer (KABATA-PENDIAS et al. 1993). The cadmium content in wheat grain was within the above standard. Cadmium in cereal grain harvested from the plots fertilized with the higher dose of N, P, K and NPK did not exceed the values established as the maximum permissible concentrations by the Act on Food and Fodder Safety of 25 August 2006 (Act... 2006) with later amendments, which corresponds to the EU regulations such as the Commission Regulation (EC) No. 466/2001 (*Regulation...* 2001) with subsequent amendments.

Cadmium appeared in varied concentrations in cereal grains during the years of the experiment (Tables 1, 2) and ranged between 0.050 and 0.120 mg kg⁻¹ in 1993 or between 0.000 and 0.054 mg kg⁻¹ in 1997 in grain of spring barley cultivated on unlimed soil. In another study (OLIVER et al. 1996), cadmium concentrations in cereal grain were even more variable.

Statistically, the cadmium content in grain of spring barley and winter wheat depended highly significantly on mineral fertilization (B), irrespective-

ly of liming, and higher levels of this element occurred after using higher NPK doses (Table 1). Increasing cadmium concentrations in cereal grain are associated with phosphorus fertilization (GORLACH, GAMBUŚ 1997, KANIUCZAK 1997) and with deposition of dust from the atmosphere on the soil surface and on plants (INDEKA, KARACZUN 2000, KABATA-PENDIAS 2002). WLNSTRAND et al. (2007) confirmed that the grain Cd concentration increased with an increasing N fertilizing rate, irrespective of the Cd concentration in soil and grain.

No evidence was found to support any statistically significant effect of liming on the cadmium content in grain of barley and wheat. However, less cadmium was found in grain of cereals cultivated on limed soil. Cadmium solubility in soil depends on soil pH (SINGH et al. 1989, GORLACH, GAMBUŚ 1996, OLIVER et al. 1996, KANIUCZAK, HAJDUK 2000, JANSSON 2002). Some research-

Table 1

Content of cadmium in grain of spring barley (mg kg^{-1} d.m.) cultivated on loessial soil (mean for 4 years)

Treatments of fertilizers (B)	A ₁		A ₂		Mean (B)
	mean	range	mean	range	
N ₀ P ₀ K ₀	0.097	0.02-0.16	0.082	0.03-0.15	0.089
N ₀ P ₁ K ₁	0.098	0.02-0.17	0.064	0.01-0.10	0.081
N _{0.5} P ₁ K ₁	0.083	0.03-0.17	0.078	0.05-0.13	0.080
N ₁ P ₁ K ₁	0.061	0.00-0.09	0.047	0.02-0.10	0.054
N _{1.5} P ₁ K ₁	0.111	0.09-0.21	0.051	0.01-0.10	0.081
N ₁ P ₀ K ₁	0.086	0.09-0.13	0.066	0.02-0.10	0.076
N ₁ P _{0.5} K ₁	0.099	0.09-0.18	0.063	0.02-0.12	0.081
N ₁ P _{1.5} K ₁	0.121	0.04-0.24	0.047	0.01-0.08	0.084
N ₁ P ₁ K ₀	0.069	0.06-0.18	0.030	0.00-0.05	0.049
N ₁ P ₁ K _{0.5}	0.050	0.06-0.11	0.047	0.05-0.10	0.048
N ₁ P ₁ K _{1.5}	0.131	0.03-0.17	0.093	0.04-0.26	0.112
N _{0.5} P _{0.5} K _{0.5}	0.150	0.09-0.18	0.119	0.05-0.31	0.134
N _{1.5} P _{1.5} K _{1.5}	0.145	0.04-0.27	0.138	0.04-0.25	0.141
N ₂ P ₂ K ₂	0.171	0.05-0.32	0.165	0.05-0.30	0.168
Mean of A	0.100	-	0.076	-	-
LSD	A = ns, B* = 0.024 AB = ns				

A₁ – NPK fertilization + Mg constans, A₂ – NPK fertilization + Mg, Ca constans,
LSD – lowest significant difference for: A – liming, B – mineral fertilization (irrespective of liming),
AB – interaction between liming and mineral fertilization, *significant at $p = 0.01$,
ns – differences not significant

ers (SINGH et al. 1989, GORLACH, GAMBUŠ 1996, OLIVER et al. 1996, KANIUCZAK 1997, JANSSON 2002) suggest that it is possible to reduce the content of cadmium in plants through liming. An increase in pH values from 4 to 5 as a result of applying burnt lime reduced the cadmium concentration in wheat grain (OLIVER et al. 1996). In most of the experiments carried out by JANSSON (2002), the cadmium content in plants depended significantly on soil pH. Our own studies did not demonstrate statistically significant interaction between liming and mineral fertilization (AB). Nonetheless, on all the fertilized objects that were limed, the cadmium content in grain of the analyzed cereals was lower, compared to grain harvested from on unlimed soil (Table 1, 2).

Table 2

Content of cadmium in grain of winter wheat (mg kg^{-1} d.m.) cultivated on loessial soil (mean for 4 years)

Treatments of fertilizers (B)	A ₁		A ₂		Mean (B)
	mean	range	mean	range	
N ₀ P ₀ K ₀	0.077	0.05-0.10	0.040	0.02-0.06	0.058
N ₀ P ₁ K ₁	0.091	0.07-0.12	0.033	0.00-0.05	0.062
N _{0.5} P ₁ K ₁	0.085	0.03-0.14	0.034	0.00-0.06	0.059
N ₁ P ₁ K ₁	0.089	0.04-0.14	0.023	0.00-0.07	0.056
N _{1.5} P ₁ K ₁	0.107	0.09-0.14	0.099	0.08-0.11	0.103
N ₁ P ₀ K ₁	0.067	0.00-0.11	0.062	0.00-0.12	0.064
N ₁ P _{0.5} K ₁	0.099	0.04-0.17	0.095	0.07-0.14	0.097
N ₁ P _{1.5} K ₁	0.103	0.07-0.14	0.068	0.01-0.11	0.085
N ₁ P ₁ K ₀	0.062	0.00-0.10	0.045	0.01-0.09	0.053
N ₁ P ₁ K _{0.5}	0.070	0.03-0.09	0.046	0.04-0.08	0.058
N ₁ P ₁ K _{1.5}	0.056	0.01-0.08	0.036	0.03-0.06	0.046
N _{0.5} P _{0.5} K _{0.5}	0.078	0.02-0.10	0.031	0.02-0.06	0.054
N _{1.5} P _{1.5} K _{1.5}	0.102	0.07-0.12	0.096	0.06-0.14	0.099
N ₂ P ₂ K ₂	0.120	0.04-0.16	0.100	0.07-0.15	0.110
Mean of A	0.086	-	0.058	-	-
LSD	A = ns, B* = 0.030 AB = ns				

A₁ – NPK fertilization + Mg constans, A₂ – NPK fertilization + Mg, Ca constans,
LSD – lowest significant difference for: A – liming, B – mineral fertilization (irrespective of liming),
AB – interaction between liming and mineral fertilization, *significant at $p = 0.01$,
ns – differences not significant

The cadmium content in grain of the examined cereals was within the range provided by some monitored research (KABATA-PENDIAS 2002, SZTEKE, BOGUSZEWSKA 2000). Among the analyzed grain, wheat grain usually accumulates more cadmium (INDEKA, KARACZUN 2000, WŁNGSTRAND et al. 2007). These values are comparable with the ones found in other European countries and in the other parts of the world.

CONCLUSIONS

1. Liming did not prove to have any significant effect on the cadmium content in grain of spring barley and winter wheat. However, in response to this treatment, the cadmium content in cereal grain tended to decline.

2. Mineral NPK fertilization, applied in higher doses, had significant impact by raising the cadmium content, especially in spring barley grain and to a lesser degree in winter wheat grain.

3. No statistical relationship was proven between liming and mineral fertilization in shaping the cadmium content in grain of spring barley or winter wheat. However, the cadmium content was generally lower in grain of cereals cultivated on fertilized objects where liming was applied.

4. The cadmium content in grains of spring barley and winter wheat, fertilized with high doses of NPK, did not exceed the level ($0.20 \text{ mg Cd kg}^{-1}$ of fresh matter) considered as the maximum permissible one in crops intended for human consumption.

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