Direct and secondary effect of liming and organic fertilization on cadmium content in soil and in vegetables

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ABSTRACT

A direct and secondary effect of liming and organic fertilization on the cadmium content in soil and in vegetables was examined. Celeriac (*Apium graveolens* L. var. *rapaceum*) was cultivated in the first year after lime application and organic fertilization whereas leek (*Allium ampeloprasum* ssp. *porrum* J. Gay) was grown in the next year. Soil was limed with a calcium carbonate fertilizer at the rate of 2.0 t CaO/ha. The following were applied as organic fertilizers: farmyard manure (60 t/ha), rye straw (4 t/ha), rye and winter vetch, both the plants cultivated as winter catch crops for green manure. Liming significantly reduced the available cadmium content in the soil in the first and second year after its application. Also, it significantly reduced the cadmium content in celeriac and leek compared with no-liming cultivation. Organic fertilization, especially farmyard manure and straw, significantly reduced the soil available cadmium content as compared to the untreated control (without organic fertilization). The aforementioned factor significantly reduced the cadmium content in the examined vegetables. Cadmium lowest content in celeriac leaves and leek was recorded after the application of farmyard manure. A combined application of liming and organic fertilization in the form of farmyard manure most beneficially influenced celeriac leaves with respect to their cadmium content.

Keywords: heavy metals; cadmium; liming; organic matter application; celeriac; leek

Among crop plants, vegetables show the highest ability to accumulate heavy metals due to the assimilation of the metals from soil by the plants, and as a result of leaf assimilation (Jasiewicz et al. 1997).

Cadmium is easily assimilated through both the root system and aboveground parts, the phenomenon indicated by high values of the soil-plant transfer index (Galler 1992).

The significant factors influencing the availability of heavy metals are soil pH and the quality of soil organic matter (Barančíková and Makovníková 2003, Puschenreiter et al. 2005).

One of the ways to counteract negative effects of soil contamination with heavy metals is to apply organic matter into polluted soil. Kuduk (1983) suggests organic fertilization in the form of farmyard manure, green manures, straw, compost, peat, organic silt from water reservoirs, and industrial wastes including wood industrial waste material. Kolář et al. (1998) and Vácha et al. (2002) suggest that the quality of organic matter application significantly influences heavy metals mobility.

Bioavailability of heavy metals is substantially limited by soil pH. According to Jackson and Alloway (1991) as well as Gołda et al. (1994) soil liming should be a basic cultivation operation, which reduces hazards following from increased contents of heavy metals in the soil. Chaney (1994) and Vácha et al. (2002) argue that soil pH most notably influences the potential toxicity of heavy metals and their assimilation by plants.

In the years 2000–2004 the Department of Vegetable Cultivation at the University of Podlasie carried out an experiment to study soil liming and organic fertilization effects on the cadmium content in soil and vegetables cultivated on it. A direct effect (in the first year) as well as a secondary impact (in the second year) of the aforementioned factors on the total and available cadmium content in soil and its concentration in edible parts of vegetable were studied.

MATERIAL AND METHODS

The aim of the study was to determine the direct and secondary effect of liming and organic fertilization on the available cadmium content in the soil and the vegetables cultivated on it. A field experiment was conducted in the years 2000–2004. It was a three-stage trial, individual stages started in the years 2000, 2001, 2002. Liming and organic fertilization was applied in the first year, in the following year the celeriac (*Apium graveolens* L. var. *rapaceum*) was cultivated, and in the third year the leek was grown (*Allium ampeloprasum* ssp. p*orrum* J. Gay).

Experiments were set up in the fields of the Experimental Farm in Zawady. They were located in the proximity of the international route E30, which is characterised by heavy road traffic. Car fumes and exploitation materials are sources of environmental pollution of the land on both sides of the road with cadmium, among others. The experiment was set up along the route at the distance of 10 m from the edge of the road. The replications were located along the road.

Research was carried out on Luvisol. The soil organic matter (SOM) content averaged 1.5% and its humus horizon reached the depth of 30–40 cm. Before the experiment set-up, soil pH determined in H_2O was 5.7. The total cadmium content in topsoil was 1.25 mg Cd/kg dm and it markedly exceeded the average content of this element in Polish soils (0.22 mg Cd/kg dm according to Terelak et al. 1995); still, it remained within the limits of acceptable cadmium content established for arable lands. The plant-available cadmium level in the topsoil averaged 0.13 mg Cd/kg dm, being 9.35% of the total Cd content.

The experimental design was split-block with three replications. The following factors were studied:

(A) soil liming:

(1) soil limed with a calcium carbonate at the rate of 2.0 t CaO/ha,
(2) non-limed soil;

(B) organic fertilization:

(1) control without organic fertilization,
(2) farmyard manure at the rate of 60 t/ha,
(3) rye straw at the rate of 4 t/ha,
(4) rye (seeding rate 220 kg/ha),
(5) hairy vetch (seeding rate 70 kg/ha).

The plot area for harvest was 12.5 m^2; the whole experiment area was 820 m^2. The experiment comprised three research stages, each initiated with soil liming and organic fertilization. In the first year after liming and fertilization, the Gol celeriac was cultivated, and in the next year the leek variety Arkansas was grown.

Soil liming was carried out in July, a month prior to hairy vetch sowing. The plants for green manure were cultivated as winter catch crops. In the years 2000–2002 vetch and rye were sown in the third decade of August and in the second decade of September, respectively. In the year that followed, green mass of the catch crops, rye straw and farmyard manure were incorporated into the soil in the first decade of May. Before incorporation samples of plant material, straw and farmyard manure were collected in order to determine their fertilizing values, which included:

(1) fresh and dry matter yield of plants grown on the limed and non-limed soil (t/ha),
(2) Cd content in the catch crop plants, farmyard manure and straw (mg/kg dm).

Celeriac was cultivated in the years 2001–2003 whereas leek was grown in the years 2002–2004. During the harvest of the vegetables representative soil samples (at the depth of 0–30 cm) and plant tissue samples were taken from each combination to determine the cadmium content.

Soil samples were collected for each investigated object from all four replications. To obtain mixed samples between ten and twenty soil pricks with Egner-Rheim rod were done by the normal technique (Namieśnik et al. 1995). The weight of each sample for laboratory analysis amounted to 0.5 kg.

In order to obtain homogeneous samples for laboratory analysis the plant material was subjected to homogenization, and the soil was crushed in the agate mortar. The plant and soil material was dried to obtain the dry matter (dm). Plant samples were ground after drying.

Available cadmium was extracted from the soil by 0.01M $CaCl_2$ solution. The total cadmium content in the soil, organic fertilizers and vegetables was determined after microwave digestion in the MILESTONE high-pressure microwave system MLS-1200 MEGA. Plant material and soil were wet-mineralised in a mixture of concentrated nitric acid and perhydrole. 0.5-g samples were taken for analysis. Then 5 ml of HNO_3 + 0.5 ml H_2O_2 concentration was added. The following programme of dilution was applied: 6 min 250 W; 6 min 400 W; 6 min 650 W; 6 min 250 W. The diluted samples were moved to the flask and 1M solution of HNO_3 was added.

Cadmium was determined after an extraction of complexes in the presence of APDC – Ammonium

Pyrrolidinedithiocarbamate (on the determination day). Cadmium content in the solutions obtained, standards [cadmium, standard solution (1000 ppm) Spectrosol BDH Laboratory Supplies, England] and the blank test were determined by the method of atomic spectrophotometry absorption.

The determination was carried out by the SOLAR 929 device produced by ATI UNICAM in the acetylene-oxygenic flame at the wavelength of 228.8 nm. Background correction with a deuterium lamp was applied. The method and analytic apparatus precision for cadmium amount to 0.01 mg/l.

The results obtained were used to calculate the following indices:

(1) bioavailability (ratio of soluble Cd content and total Cd content),

(2) bioaccumulation (ratio of Cd content in vegetables and total Cd content in soil).

The results were statistically analysed by means of the analysis of variance following the mathematical model for the split-block design. Significance of differences was determined by the Tukey test at the significance level of $P = 0.05$.

RESULTS AND DISCUSSION

Fertilizing value of catch crop plants, farmyard manure and straw

Among the examined organic fertilizers, the largest amounts of fresh and dry matter were incorporated into the soil with farmyard manure (Table 1). Rye fresh matter yield was significantly higher than the fresh matter yield of vetch. Rye catch crop introduced almost twice as much fresh matter and more than twice as much dry matter as hairy vetch.

Statistically significant interaction of soil liming and plant species cultivated for green manure was proved. Rye fresh and dry matter yield was significantly higher in the limed than in the non-limed soil. Hairy vetch grown on limed and non-limed soils produced similar fresh and dry matter yields.

The organic fertilizers studied were characterised by low cadmium content (Table 1). 60 t of farmyard manure introduced 10.71 g Cd/ha whereas 4 t of straw introduced 1.02 g Cd/ha. The catch crop plants (mainly rye) grown on the non-limed soil introduced more cadmium into the soil than the plants cultivated on the non-limed soil.

Effect of soil liming and organic fertilization on soil cadmium content

Direct effect. In the first year after liming and organic fertilization, the cadmium total content in the soil averaged 1.25 mg Cd/kg dm and was not significantly different for the investigated treatments (Table 2).

An average content of cadmium available for plants at celeriac harvest was at the level of 0.13 mg Cd/kg dm (Table 2). Both soil liming and organic fertilization reduced the available cadmium

Table 1. Amount of organic matter and cadmium introduced into the soil with organic fertilizers (means for years 2001–2003)

Organic fertilization	Fresh matter (t/ha)		Dry matter (t/ha)		Cadmium (g/ha)	
	LS	NLS	LS	NLS	LS	NLS
Farmyard manure	60.00	60.00	16.13	16.19	10.71	10.71
Rye straw	4.00	4.00	3.31	3.38	1.02	1.02
Rye	23.46	26.27	5.63	6.43	13.28	17.37
Hairy vetch	13.57	13.52	2.89	2.82	4.57	4.73
Mean	25.26	25.95	6.99	7.21	7.40	8.46
LSD ($P = 0.05$) for						
soil liming	0.40		0.16		0.87	
organic fertilization	1.07		0.32		0.78	
interaction	0.98		0.35		2.01	

LS = limed soil; NLS = non-limed soil; n.s. = not significant

Table 2. The cadmium content in soil in the first year after soil liming and organic fertilization (means for years 2001–2003)

Organic fertilization	Total cadmium (mg Cd/kg dm)		Available cadmium (mg Cd/kg dm)		Bioavailability (%)	
	LS	NLS	LS	NLS	LS	NLS
Control	1.25	1.24	0.13	0.14	10.5	11.3
Farmyard manure	1.25	1.25	0.11	0.12	8.9	9.8
Rye straw	1.24	1.26	0.12	0.13	9.7	10.4
Rye	1.25	1.24	0.11	0.12	8.8	9.8
Hairy vetch	1.24	1.25	0.12	0.13	9.8	10.6
Mean	1.25	1.25	0.12	0.13	9.5	10.4
LSD (P = 0.05) for						
soil liming	n.s.		0.01		0.6	
organic fertilization	n.s.		0.01		0.8	
interaction	n.s.		n.s.		n.s.	

LS = limed soil; NLS = non-limed soil; n.s. = not significant

content so the effect of both operations was beneficial. A significant drop in the available Cd content was found in the limed soil when compared to the non-limed soil. All the experimental organic fertilizers contributed to the available cadmium content reduction in the soil compared with the control. Farmyard manure- and rye catch crop-fertilized soils contained less available cadmium than the rye- and hairy vetch-fertilized soils.

Table 2 also presents numerical data of the values of cadmium availability index (bioavailability) in the first year after soil liming and organic fertilization. In the soil sampled at celeriac harvest, an average of 10% cadmium was in the form of plant available compounds. Their amount was significantly reduced by soil liming as the limed soil contained by 0.9% less available cadmium compared with the non-limed soil.

Table 3. The cadmium content in soil in the second year after soil liming and organic fertilization (means for years 2002–2004)

Organic fertilization	Total cadmium (mg Cd/ha dm)		Available cadmium (mg Cd/ha dm)		Bioavailability (%)	
	LS	NLS	LS	NLS	LS	NLS
Control	1.24	1.24	0.14	0.14	10.1	10.6
Farmyard manure	1.26	1.26	0.12	0.13	9.0	9.4
Rye straw	1.61	1.25	0.13	0.14	9.6	10.5
Rye	1.24	1.25	0.12	0.13	9.3	9.6
Hairy vetch	1.26	1.25	0.14	0.14	10.2	10.5
Mean	1.26	1.25	0.13	0.14	9.6	10.1
LSD (P = 0.05) for						
soil liming	n.s.		0.01		0.2	
organic fertilization	n.s.		0.01		0.7	
interaction	n.s.		n.s.		n.s.	

LS = limed soil; NLS = non-limed soil; n.s. = not significant

Farmyard manure, rye straw and rye catch crop fertilization significantly reduced the available cadmium share in the total Cd content as compared to the share recorded for organically non-fertilized soil. Farmyard manure and rye significantly reduced the available Cd share compared with hairy vetch and straw and hairy vetch, respectively.

Secondary effect. In the second year after soil liming and organic fertilization the total cadmium content amounted to 1.26 mg Cd/kg (Table 3). Just like in the first year, no significant differences between the investigated treatments were found.

The plant-available cadmium content was 0.13 mg Cd/kg (Table 3). A secondary effect of the factors examined in the experiment substantially influenced the available cadmium content in soil. The limed soil contained significantly less available cadmium than the non-limed soil.

Beneficial farmyard manure and rye catch crop influences on the available cadmium content lasted throughout the second year after organic fertilization. The soil amended with the fertilizers organic mass contained significantly less available cadmium forms than the organically non-limed soil as well as the soil fertilized with rye straw and hairy vetch catch crop.

In the second year after soil liming and organic fertilization, an available cadmium percentage share in the total Cd content averaged 9.9% (Table 3). It was found to be significantly lower in the limed soil compared with the non-limed soil. A secondary impact of organic fertilization on the Cd share was also proved. The lowest value of cadmium bioavailability was typical for the farmyard manure-fertilized soil and it was significantly lower than the rye straw- and vetch-fertilized soil as well as organically non-fertilized soil.

Soil liming and organic fertilization effects on the cadmium content of vegetables

Direct effect. An average cadmium content in storage roots and leaves of celeriac cultivated in the first year after soil liming and organic fertilization amounted to 1.42 mg Cd/kg dm and 1.17 mg Cd/kg dm, respectively (Table 4).

An interaction of both investigated factors was found with respect to the cadmium content in celeriac storage roots. The lowest cadmium content was detected after farmyard manure incorporation into the limed soil. The roots of celeriac cultivated after rye catch crop contained significantly less cadmium compared with the vegetable grown on straw- and vetch-fertilized soils as well as organically non-fertilized plots. Rye straw and vetch catch crop incorporation did not yield significant reduction of cadmium amount in celeriac roots as compared to the control treatment. In contrast, all the organic fertilizers applied on the non-limed soil significantly limited cadmium absorption compared to the control combination. The roots of celeriac grown after farmyard manure and rye catch crop incorporation contained less cadmium than the roots harvested on the rye straw-amended plots.

The celeriac grown on limed soil contained significantly less cadmium in roots and leaves than the vegetable grown on non-limed soil.

All the organic fertilizers examined in the experiment reduced the cadmium content in celeriac leaves, compared to the control combination. The lowest level of this metal in leaves was recorded on farmyard manure-fertilized plots. It was significantly higher after rye straw and vetch application.

The cadmium bioaccumulation averaged 1.14 and 1.00 for celeriac storage roots and leaves, respectively (Table 4). Celeriac cultivated on the non-limed soil had a significantly higher value of bioaccumulation than the plant grown on the limed soil.

The highest values of bioaccumulation were characteristic for the roots and leaves of celeriac grown without organic fertilization whereas the lowest values were found for farmyard manure-fertilized celeriac. Compared with the control treatment, incorporation of all the organic fertilizers reduced values of cadmium bioaccumulation for celeriac.

Secondary effect. The cadmium content in white and green parts of leek cultivated in the second year after soil liming and organic fertilization amounted to 1.30 mg Cd/kg dm, on average (Table 5).

A secondary effect of soil liming on the amount of cadmium assimilated by leek was found. The white and green parts of leek cultivated on the limed soil contained significantly less cadmium as compared to the leek grown on the non-limed soil.

Values of cadmium accumulation indices for leek white and green parts indicate a beneficial secondary effect of liming. Leek grown on the limed soil had significantly lower values of these indices compared to the values obtained for the leek harvested from non-limed plots.

Organic fertilization showed a significant secondary effect, too. The highest cadmium amount in

Table 4. Cadmium content and cadmium accumulation rate in celeriac cultivated in the first year after soil liming and organic fertilization (means for years 2001–2003)

Organic fertilization	Cadmium content (mg Cd/kg dm)		Bioaccumulation	
	LS	NLS	LS	NLS
Storage roots				
Control	1.48	1.62	1.18	1.31
Farmyard manure	1.22	1.36	0.97	1.09
Rye straw	1.41	1.52	1.15	1.21
Rye	1.31	1.42	1.05	1.15
Hairy vetch	1.42	1.44	1.15	1.16
Mean	1.37	1.47	1.10	1.18
LSD (P = 0.05) for				
soil liming	0.03		0.02	
organic fertilization	0.10		0.09	
interaction	0.09		n.s.	
Leaves				
Control	1.25	1.32	1.06	1.14
Farmyard manure	1.05	1.14	0.87	0.93
Rye straw	1.09	1.19	0.96	1.01
Rye	1.07	1.16	0.89	1.02
Hairy vetch	1.17	1.26	1.00	1.09
Mean	1.12	1.21	0.96	1.04
LSD (P = 0.05) for				
soil liming	0.03		0.03	
organic fertilization	0.05		0.04	
interaction	n.s.		n.s.	

LS = limed soil; NLS = non-limed soil; n.s. = not significant

leek edible parts was characteristic for the plants cultivated in the second year after hairy vetch incorporation, and with no organic fertilization. In the second year after incorporation, farmyard manure significantly reduced the cadmium content in leek green parts whereas farmyard manure and rye catch crop showed the same effect on its white parts, compared to the control.

Organic fertilization also significantly influenced the value of cadmium bioaccumulation (Table 5). It was significantly lower for the white parts of leek fertilized with farmyard manure and rye green manure as compared to the index calculated for hairy vetch fertilization as well as no fertilization. The value of the bioaccumulation for straw-fertilized leek white parts was similar to the value for rye-fertilized leek and significantly higher than the value for the leek cultivated without farmyard manure application. The highest value of bioaccumulation for leek green parts was obtained in the case of the cultivation excluding organic fertilization, and it was significantly higher than the value of the index calculated with respect to farmyard manure fertilization.

The results of the research showed a beneficial direct and secondary effect of soil liming on the plant-available cadmium content in the soil. At celeriac and leek harvests, limed soil contained significantly less available cadmium than the non-limed soil. It is also reflected in availability index values. The results obtained are similar to the results reported by other investigators. Baran et al. (1998) states that light soil liming with calcium carbonate, increasing the soil pH value, is

Table 5. Cadmium content and cadmium accumulation rate in leek cultivated in the second year after soil liming and organic fertilization (means for years 2002–2004)

Organic fertilization	Cadmium content (mg Cd/kg dm)		Bioaccumulation	
	LS	NLS	LS	NLS
White part				
Control	1.34	1.39	1.00	1.04
Farmyard manure	1.14	1.21	0.83	0.90
Rye straw	1.29	1.37	0.92	1.01
Rye	1.22	1.28	0.91	0.95
Hairy vetch	1.37	1.38	1.01	1.02
Mean	1.27	1.33	0.93	0.98
LSD (P = 0.05) for				
soil liming	0.02		0.03	
organic fertilization	0.06		0.06	
interaction	n.s.		n.s.	
Green part				
Control	1.31	1.35	0.98	1.00
Farmyard manure	1.22	1.29	0.90	0.95
Rye straw	1.29	1.34	0.92	1.00
Rye	1.24	1.29	0.93	0.96
Hairy vetch	1.31	1.35	0.97	0.99
Mean	1.27	1.33	0.94	0.98
LSD (P = 0.05) for				
soil liming	0.02		0.02	
organic fertilization	0.07		0.06	
interaction	n.s.		n.s.	

LS = limed soil; NLS = non-limed soil; n.s. = not significant

an effective method of limiting solubility of heavy metals. Niemyska-Łukaszuk (1995) suggests that the plant-available cadmium content in soil, expressed as an Cd percentage share in the total Cd content, at pH ranging from 6.1 to 6.5, decreases up to a level lower than 1% whereas, at pH equal to 6.5, soil available cadmium is not present at all. A significant relationship between cadmium solubility and availability for plants, and soil pH is also mentioned by Chłopecka et al. (1996) and Young et al. (2000).

Soil liming reduced the cadmium content in celeriac over the first year, and in leek over the second year after lime application. Niemyska-Łukaszuk (1995), Tlustoš et al. (1995) and Lombi et al. (2002) pointed to a limiting effect of soil pH regulation on phytoavailability of heavy metals. Kuziemska and Kalembasa (1997) found that soil liming reduced the Cd content in maize, barley, wheat and red clover. Also Sauerbeck (1991) and Chaney (1994) agreed that plant cadmium content is closely connected with soil pH.

The applied organic fertilization, in particular farmyard manure and rye catch crop, significantly reduced the available cadmium content in soil in the first and second year after incorporation. The calculated availability indices indicate a direct and secondary reducing effect of the above-mentioned fertilizers on decreasing the amount of available cadmium content in soil. A significant effect of organic matter incorporation on cadmium solubility and limitation of Cd uptake by plants is also reported by Bjerre and Schierup (1985), and Woźniak (2000). Gondek and Filipek-Mazur (2005) reported that the effect of organic matter on the cadmium mobility is more pronounced in the first year after its application, whereas in the second and third year it is continually reduced. In contrast, Vácha et al. (2002) showed that an application of high doses of farmyard manure and green manure increased the mobility of heavy metals in the soil. Krishnamurti et al. (1997) argue that organic acids secreted by roots of some plant increase solubility of soil elements including heavy metals.

Organic fertilization facilitated reduction of the cadmium content in the tested vegetables. Compared with the control, the cadmium content in celeriac storage roots was significantly lower after an application of all the organic fertilizers, excluding straw. In celeriac leaves, a significant drop in the cadmium amount was recorded after fertilization with all the organic fertilizers, as compared to the control.

The coefficient of cadmium accumulation in the celeriac roots amounted from 0.97 after farmyard manure on the limed soil to 1.31 on the control without liming. Machelett et al. (1993) reports that the coefficient of cadmium transfer from soil to the celeriac storage roots and leaves amounts to 2.09 and 2.89, respectively.

A beneficial secondary reducing effect on the cadmium content in leek edible parts was characteristic for farmyard manure and rye catch organic fertilizers.

Narwal et al. (1992) showed that farmyard manure incorporation into the soil significantly reduced the cadmium content in carrot, spinach and wheat. Curyło and Jasiewicz (1997) found that an organic and mineral fertilizer including fine brown coal fractions limited cadmium uptake by vegetables, compared with mineral fertilization only. Kiepas-Kokot et al. (2000) noted a beneficial effect of organic matter incorporated into the soil in the form of vermicompost on cadmium concentration in radish seedlings.

In the present study, more favourable influence of organic fertilizers was observed on non-limed soil. In a 41-year experiment, Mineev and Gomonova (1993) proved that a combined application of mineral and organic fertilization and liming beneficially influenced phytoavailability of heavy metals, including cadmium, by vegetables. Similar results were obtained by Ristovic (1995) who reported a drop in the cadmium content in lucerne and lettuce following combined farmyard manure and calcium carbonate fertilization.

An average value of cadmium accumulation index was 1.14 for celeriac storage roots, 1.00 for celeriac leaves and 0.96 for leek white as well as green parts. The value of this index computed for celeriac indicates that cadmium content in the vegetable may exceed the metal concentration in the soil. According to Alloway and Ayres (1999) the ratio of plant and soil cadmium contents is within the limits of 1 to 10.

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