

CONCENTRATION OF LEAD AND CADMIUM IN SELECTED VEGETABLES GROWN IN THE REGION OF WARMIA AND MAZURY

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The study reports on the amount of lead and cadmium in selected samples of vegetables obtained directly from Warmian-Masurian producers, and commercial samples from a deep-frozen food producer. Concentration of analysed compounds after dry mineralisation of biological material and organic phase extraction (APDC/MBIK) has been determined using the atomic absorption spectrophotometry (AAS) in a UNICAM 939 AA apparatus.

There has been significantly high concentration of lead in the samples of cauliflower (0.95 mg/kg) and carrot (0.98 mg/kg). In commercial samples the difference was statistically significant. Whereas significantly higher concentration of cadmium has been detected in spinach both in producer and commercial samples (0.092 and 0.086 mg/kg respectively). Generally, concentration of metals determined was similar in vegetable samples obtained from the suppliers and in commercial ones.

The researched vegetables were characterised by lower concentration of particular compounds compared to valid legal regulations.

INTRODUCTION

Owing to their nutritive value fruit and vegetables are a significant component in human diet. Except for mineral compounds, vitamins or cellulose they can also contain compounds from a polluted environment. Several heavy metals such as lead or cadmium are particularly dangerous owing to their ability to accumulate in a human organism [Lo Coco *et al.*, 2000; Marzec & Schlegel-Zawadzka, 2004]. According to many authors [Jasiewicz *et al.*, 1998; Tyksiński *et al.*, 1993; Wiśniowska-Kielian, 2000], concentration of heavy metals within soil depends on several natural and anthropogenic factors. Zaniewicz-Bajkowska *et al.* [1999] claims that one of the methods of disabling heavy metals and decreasing their absorption from soil is to enrich the soil with organic matter by organic fertilisation.

However, low concentrations of metals within soil do not mean relatively low concentrations within plants. The pH of soil has got a significant influence on the amount of lead and cadmium absorbed by plants. Contaminants in acidic soil pervade more intensively than in inert soil. With reference to data published in literature, one third of Polish soil is over acidified (pH < 5.5) [Report 2001]. According to Polish authors' data [Marzec *et al.*, 2004], vegetables and grain products are the main sources of lead and cadmium in human adults' diet. The authors have estimated that vegetables bring 26.9% of cadmium and 26.8% of lead into one-day food ration. Therefore, it is necessary to continuously monitor the

safety of vegetables. In EU countries acceptable chemical contaminant levels are determined in Commission Regulation [2001]. Particularly low acceptable contaminant levels apply to the fruit and vegetables from which products for infants and children are made.

The objectives of the following dissertation have been: to determine whether the vegetables from the Warmian-Masurian region are harmless in relation to their lead and cadmium content, and to determine concentration of the researched compounds depending on the vegetable type.

MATERIAL AND METHODS

The researched material consisted of samples of vegetables such as carrot, cauliflower, broccoli, green pea, haricot bean and spinach. Both samples from suppliers (Table 1) and commercial samples (Table 2) have been examined. The samples have been drawn from 10 producers (suppliers) from the Eastern Poland region. The producers were individual farmers supplying vegetables to enterprise producing frozen vegetables. Altogether, 180 supplier and 72 commercial samples (being market products) have been examined. The samples (approximately 2000 g each) were collected during 2003 and 2004 years, frozen and kept at -25°C until analysed.

Concentration of lead and cadmium after dry mineralisation of biological material (30 g of homogenized samples) and organic phase extraction (APDC/MBIK) has been determined using the atomic absorption spectrophotometry (AAS)

in a UNICAM 939 AA apparatus, equipped in datastation Adax and background correction.

Differences in the levels of the metals between particular vegetables were tested by the use of one-way analysis of variance (ANOVA). The significance differences were examined with the Tukey's test at the significance level of $p=0.05$ with the use of Statistica 6.0 software.

RESULTS AND DISCUSSION

Concentrations of lead and cadmium in researched vegetables coming from suppliers (producers) have been shown in Table 1. The highest concentrations can be observed in carrot (average of 0.981 ± 0.028 , ranging from 0.065 to 0.148 mg/kg) and cauliflower (average of 0.950 ± 0.041 , ranging from 0.070 to 0.166 mg/kg). However, in this instance, determined values have been significantly higher comparing to other vegetable types.

Concentrations of cadmium in supplier (Table 1) and commercial (Table 2) samples of particular vegetables have been at similar levels. Significantly higher amount of cadmium have been determined in spinach: an average of 0.092 ± 0.020 , ranging from 0.066 to 0.115 mg/kg in supplier samples and 0.086 ± 0.025 , ranging from 0.055 to 0.123 mg/kg in producer samples. It has been determined that the amount of cadmium in commercial samples of carrot differed significantly from the amount in the other vegetables.

In accordance with the EU Commission Decree [Commission Regulation 2001], which is valid in Poland, concentration of lead should not exceed 0.1-0.2 mg/kg, depending on the kind of vegetable while the amount of cadmium should range from 0.05 to 0.2 mg/kg. In researched vegetables the permissible values have not been exceeded. Little data concerning the level of heavy metal contamination of vegetables cultivated in other European countries is there in available literature. Therefore, discussing the obtained results is quite difficult.

Data published by Polish authors applies mainly to lead and cadmium concentration in carrot. The values obtained

in this experimental work are much lower than the data published within last decades. According to literature, concentrations of metals in carrot from the polluted Silesian regions of Poland [Śmigiel *et al.*, 1993] could be of high levels (lead – 0.19, cadmium – 0.05 mg/kg). Other authors [Kowalska-Pyłka *et al.*, 1995; Tyksiński *et al.*, 1993; Kocjan *et al.*, 2002] have also determined higher, compared to results obtained here, concentrations of these metals in carrot originating from areas neighbouring other Polish cities: Poznan, Stalowa Wola, Lublin. Results of monitoring research carried out in Poland [Report, 2002] show that average amounts of lead and cadmium in carrot in 2001 were 0.05 (ranging from 0.01 to 0.28) and 0.047 (ranging from 0.002 to 0.268 mg/kg) respectively.

Data published in Report [2001] indicates that Polish soils are less heavy-metal contaminated comparing to soils in other countries in the world. Investigations that have been made confirm that Warmian-Masurian region of Poland is ecologically clean.

Sękara *et al.* [2005] determined the cadmium and lead accumulation and distribution in the plants' organs. The red beet characterized by the highest cadmium and lead concentrations ratio shoots/roots. According to authors the phytoremediation efficiency of the investigated crops depended on the biomass production and the possibility of metal accumulation in harvestable organs. Also, Spanish authors [Peris *et al.*, 2007] analysed heavy metal content in the edible parts of two types of horticultural crops (leaf and inflorescence crops). The results showed a higher absorption and accumulation of heavy metals in leaf crops than in inflorescence crops.

CONCLUSIONS

1. Results of the research indicate little, trace lead and cadmium contamination of vegetables produced in the Warmian-Masurian region of Poland. Similar amounts of metals have been obtained from producer and commercial samples, which proves that freezing process does not influence their concentrations.

TABLE 1. Contents of lead and cadmium (mg/kg) in vegetable samples originating from suppliers.

Vegetable	Element	$\bar{X} \pm SD$	Range
Carrot	Pb	$0.962^a \pm 0.014$	0.094 – 0.135
	Cd	$0.023^a \pm 0.003$	0.020 – 0.027
Spinach	Pb	$0.058^b \pm 0.016$	0.040 – 0.083
	Cd	$0.092^b \pm 0.020$	0.066 – 0.115
Cauliflower	Pb	$0.943^a \pm 0.022$	0.072 – 0.128
	Cd	$0.010^a \pm 0.002$	0.009 – 0.013
Broccoli	Pb	$0.060^a \pm 0.014$	0.041 – 0.072
	Cd	$0.009^a \pm 0.001$	0.007 – 0.010
Green pea	Pb	$0.084^b \pm 0.035$	0.033 – 0.132
	Cd	$0.009^a \pm 0.001$	0.007 – 0.011
Haricot bean	Pb	$0.056^a \pm 0.011$	0.043 – 0.072
	Cd	$0.004^a \pm 0.001$	0.003 – 0.006

a,b: statistically significant difference at $p < 0.05$.

TABLE 2. Contents of lead and cadmium (mg/kg) in vegetable samples originating from commercial samples.

Vegetable	Element	$\bar{X} \pm SD$	Range
Carrot	Pb	$0.981^a \pm 0.028$	0.065 – 0.148
	Cd	$0.019^a \pm 0.006$	0.015 – 0.027
Spinach	Pb	$0.062^b \pm 0.040$	0.026 – 0.134
	Cd	$0.086^b \pm 0.025$	0.055 – 0.123
Cauliflower	Pb	$0.950^a \pm 0.041$	0.070 – 0.166
	Cd	$0.008^c \pm 0.002$	0.005 – 0.011
Broccoli	Pb	$0.065^b \pm 0.028$	0.043 – 0.120
	Cd	$0.008^c \pm 0.003$	0.007 – 0.014
Green pea	Pb	$0.074^b \pm 0.025$	0.043 – 0.113
	Cd	$0.008^c \pm 0.003$	0.004 – 0.012
Haricot bean	Pb	$0.085^b \pm 0.011$	0.071 – 0.094
	Cd	$0.005^c \pm 0.002$	0.002 – 0.008

a,b,c: statistically significant difference at $p < 0.05$.

2. Among the analysed vegetables, carrot and cauliflower samples contained higher concentrations of lead. Whereas spinach contained the highest concentrations of cadmium. Values determined here have been lower comparing to the ones from available literature. This fact can be significant for the development of ecological agriculture in this region.

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STĘŻENIA OŁOWIU I KADMU W WYBRANYCH WARZYWACH POCHODZĄCYCH Z REGIONU WARMII I MAZUR

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W pracy określono zawartości ołowiu i kadmu w wybranych próbkach warzyw pochodzących bezpośrednio od warmińsko-mazurskich producentów oraz w próbkach handlowych, pochodzących z zakładu produkującego mrożonki. Poziomy badanych związków po mineralizacji materiału biologicznego na sucho i ekstrakcji do fazy organicznej (APDC/MIBK) oznaczono metodą spektrofotometrii absorpcji atomowej w płomieniu, przy zastosowaniu aparatu UNICAM 939 AA.

Istotnie wyższymi koncentracjami ołowiu charakteryzowały się próbki marchwi (0,98 mg/kg) i kalafiora (0,95 mg/kg), przy czym w próbkach handlowych różnice te były statystycznie istotne. Natomiast istotnie wyższe zawartości kadmu zarówno w próbkach od producentów jak i w próbkach handlowych stwierdzono w szpinaku odpowiednio 0,092 i 0,086 mg/kg. Generalnie koncentracja oznaczonych metali w próbkach warzyw od dostawców była podobna do ich stężeń oznaczonych w próbkach handlowych.

Badane warzywa charakteryzowały się niższymi, w porównaniu do obowiązujących unormowań prawnych poziomami badanych związków.