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Letter to the Editor

Cadmium and Lead Content in Cereal Grains and Soil from Cropland Adjacent to Roadways

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Abstract

The Warmia and Mazury District (northeastern Poland) is oriented towards agro-forestry and is less populated then other regions of Poland. The main objective of the present study was to characterize the effects of road traffic (road S 51) on an increase in the concentrations of lead and cadmium in the soil surface layer and cereal grains (wheat and barley grown on an experimental farm). The concentrations of lead and cadmium were determined in the studied material by atomic absorption spectrometry, following dry mineralization. The highest lead concentration was observed in soil samples collected at the starting point of sampling (10 m from the roadway edge). Road traffic load had no effect on lead concentration in the soil surface layer in samples taken more than 80 m from the road. Cadmium concentration in the soil did not depend on distance from the roadway. It was shown that differences in mean concentrations of lead and cadmium in barley and wheat grains were statistically significant. Lead and cadmium concentrations in all soil and grain samples analyzed were much lower than the maximum allowable levels in Poland of chemical impurities that can be present in foodstuffs and soils used for agricultural purposes.

Keywords: lead, cadmium, wheat , barley, soil, northeastern Poland

Introduction

One of the main consequences of industrial activities are changes in the chemical composition of particular environmental components. With regard to their persistence in ecosystems, the chemical compounds emitted may be divided into easily degradable or stable, that can be accumulated in living organisms. The first group contributes to an increase in the primary productivity of ecosystems and long-term changes in its structure. The other group includes toxic compounds capable of long-term persistence in biological systems. Toxic substances and ions destroy or damage cell structures, leading to metabolic disturbances, enzyme inhibition and modifications in photosynthesis and plant biomass distribution [1, 2].

The emission of anthropogenic heavy metal compounds causes considerable changes in biogeochemical cycles of some elements. Following their uptake from contaminated soils by food plants, heavy metals are included in the human food chain. Furthermore, heavy metal accumulation in plants evokes their stress responses. This leads to changes in chemical composition, reflected by biogenic amines accumulation, e. g. betaine, putrescine and spermine in barley [3].

Due to the fact that until the end of the 1980s petrol contained tetraethyl lead Pb $(C_2H_5)_4$, road transport was the major source of atmospheric emission of such lead

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compounds as: lead (II) chloride $PbCl_2$, lead (II) bromide-chloride PbBrCl, lead (II) chloride-hydroxide Pb(OH)Cl and lead II bis(oxide)-bromide-chloride $(PbO)_2$ PbBrCl. Most of them are unstable compounds. Several hours after emission, the following compounds are usually present: lead II bis(oxide)-carbonate $(PbO)_2PbCO_3$, lead (II) carbonate $PbCO_3$, lead (II) bromide-chloride PbBrCl, and lead oxides PbO_x [4]. Lead (II) oxide PbO and lead (IV) oxide PbO_2 are sparingly water-soluble. In slightly acid media (e. g. in the presence of diluted sulfuric and hydrochloric acids) they do not pass into the solution, forming sparingly soluble salts ($PbCl_2$ and $PbSO_4$). However, the ionic form of lead existing in the soil is taken up by plants and is accumulated mainly in their roots [5-7]. The addition of synthetic chelates highly increases lead uptake from the soil, which is used in its phytoextraction in industrial areas [8,9]. In the presence of phosphates lead forms lead phosphates, which often increases phosphorus deficit in the soil and plant organs. Some lead ions form in the soil combinations with organic compounds, hardly available to plants [10]. Due to problems with lead uptake by the root system and its penetration through internal leaf cells, one of the major sources of this element are atmospheric dusts adsorbed on the outer plant surface [5-7, 11].

Cadmium is a heavy metal characterized by high mobility in biological systems. It is emitted to the atmosphere in combustion processes, mainly in the form of oxides. In the arable soil its major sources are phosphorus fertilizers, industrial and car exhausts [1]. Cadmium uptake by plants is partly limited by the presence of calcium, phosphorus and chelating compounds in the soil [7]. Nevertheless, its ionic form is easily absorbed by roots and transported inside plants, especially in acid media. Cadmium from dust deposition is accumulated in leaves. In some tree species, cadmium concentration coefficients are higher than 200 [12]. Cadmium induces oxidative stress in plant cells and inactivates some enzymes [13].

The transformation of mineral compounds into biologically active forms, and the accumulation of elements in particular plant parts are of primary importance in plant-based foodstuff and feedstuff production. This especially concerns cadmium compounds, characterized by high mobility in the air-soil-plant system.

The main objective of the present study was to determine the concentrations of lead and cadmium in barley grain, wheat grain and soil samples collected from cropland in a non-industrial area adjacent to a heavily-trafficked road.

Materials and Methods

Samples

The lead and cadmium contents were determined in cereal grain samples collected in August 2003, and in soil samples taken on an experimental farm in Tomaszkowo, University of Warmia and Mazury. The farm is located about 6 km from the administrative boundaries of the city of Olsztyn. The sample arable land covers about 30 ha and is adjacent to Road S 51 Olsztyn-Olsztynek (central part of the Warmia and Mazury Province). According to daily measurements, traffic load is approx. 8,000 vehicles (including almost 6,000 passenger-cars and microbuses). In summer it increases to approx. 9,000 vehicles per day.

The experimental material was the grain of winter wheat (*Triticum aestivum* L. cv. Kobra) and spring barley (*Hordeum vulgare* L. cv. Start). Samples were collected with a grain combine, 10 m from the roadway edge, and then every 25 m to a distance of 310 m. The moisture content of grain was from 12.1 to 12.5%. Three samples of barley and wheat grain were taken at each distance. Also, three samples of soil surface layer (0 to 20 cm) were taken within the same belts. The soils were light and medium-heavy, slightly acid to acid, with the fraction < 0.02 mm size content from 20 to 30%. Their pH (measured with a potentiometer in a suspension of a 1 mol dm^{-3} KCl solution) was between 5.1 to 5.8. Analyses made by Chemical-Agricultural Stations show that in northeastern Poland over 44% of soils are acid soils [14].

Chemical Analysis

The heavy metal content of plants was determined after dry-ashing. Grain samples (20-30 g) were placed into quartz crucibles and mineralized thermally in a muffle furnace at 450°C [10,15]. The complexing agent was a 2% aqueous solution of ammonium pyrrolidine-dithiocarbamate (APDC). Metal complexes were extracted to the organic phase with 4-methyl-pentan-2-on (MIBK) [16, 17].

To determine the concentrations of lead and cadmium in the soil, 5 g soil samples were air-dried, ground in an agate mortar and placed in quartz crucibles. After mineralization at 450°C, the residue after ignition was etched with a mixture of concentrated nitric acid (HNO_3, d = 1.40) and perchloric acid ($HClO_4$, 70%) [10].

Lead and cadmium concentrations were determined by flame atomic absorption spectrometry (AAS) with a PYE UNICAM 939/959 Solar AA apparatus with background correction. The elements were analyzed at the Central Analytical Laboratory, University of Warmia and Mazury in Olsztyn. The method of analysis was verified with certi-

Table 1. Results of analysis of reference materials.

	Pb mg kg^{-1} dry matter		Cd mg kg^{-1} dry matter	
Material	Certified	Determined	Certified	Determined
Mixed Polish herbs INCT-MPH-2	2.16 ± 0.23	1.98 ± 0.31	0.199 ± 0.015	0.205 ± 0.020
Tea leaves INCT-TL-1	1.78 ± 0.24	1.64 ± 0.18	0.030 ± 0.004	0.027 ± 0.003

fied reference materials: Mixed Polish Herbs (INCT-MPH-2) and Tea Leaves (INCT-TL-1) from the Institute of Nuclear Chemistry and Technology, Warsaw (Table 1). Detection limits were: Cd, 0.003 mg kg^{-1}; Pb, 0.04 mg kg^{-1}.

Statistical Analysis

The results were analyzed statistically using the PRISM 4 program (GraphPad Software, Inc.). The significance of differences between concentrations of lead and cadmium in wheat and barley grain was determined with an unpaired t test.

Results and Discussion

The lead concentration in cereal grain and soil samples is presented in Table 2. The lead concentration was on average about 50% higher in the soil belt located 10 to 60 m from the roadway edge, compared with the value determined in samples obtained from longer distances. The lead concentration decreased with an increasing distance from the road, from a maximum of 11.89 mg kg^{-1} (soil sample taken very close to the road) to a minimum of 4.58 mg kg^{-1} (soil sample taken 285 m from the road) (Fig. 1). The lead accumulation indicators in the soil from cropland located 60 m from the roadway edge were determined in relation to the so-called geochemical background (the reference points were soil samples collected more than 110 m from the road). Their values ranged from 2.2 to 1.2, whereas those reported by Czarnowska [18] for soils along city arteries were much higher, i. e. 11 to 36 (on average 19.1). The maximum pollutant range of the Olsztyn-Olsztynek road, affecting an increase in the soil concentration of lead, was about 80 m (Fig. 1).

The lead concentrations determined in the soil surface layer, regardless of the distance from the road, were much lower than its mean content considered natural in uncontaminated soils (<20 mg kg^{-1}) and in arable soils (15.0 mg kg^{-1}) in the year 2000 in Poland [14]. The data provided by the Inspectorate for Environmental Protection [19] on environmental condition in the Warmia and Mazury District show that the mean lead concentration in soil samples taken along the same road (25 to 50 m) was 11.5 mg kg^{-1} in 1990, and 10.5 mg kg^{-1} in 1996, and was slightly higher than the value recorded in the present experiment (8.26 mg kg^{-1}). This difference may result from different sampling sites, topographic features, presence or absence of shrubs and trees at the roadway, different agricultural methods, and the fact that petrol used today has a reduced lead content. The mean lead concentration in the soil beyond the road effect was very low (5.40 mg kg^{-1}), almost twofold lower than the control adopted by Czarnowska [11,18] in her studies on the effects of means of transportation on the chemical composition of soils.

The mean lead concentration in wheat grain amounted to 0.060 mg kg^{-1}, and in barley grain — to 0.081 mg

Table 2. Lead and cadmium content of wheat, barley and soil samples (mg kg^{-1} dry matter)

	Sample	N	Mean	SD	Min.	Max.
Lead	Wheat	39	0.060***	0.012	0.04	0.09
	Barley	39	0.081***	0.014	0.06	0.12
	Soil[a]	12	8.26	1.93	6.33	11.89
	Soil[b]	30	5.40	0.48	4.58	6.23
Cadmium	Wheat	39	0.025***	0.007	0.015	0.040
	Barley	39	0.041***	0.011	0.020	0.064
	Soil	42	0.015	0.008	0.003	0.032

[a] Mean value for measurements of samples taken 10, 35 and 60 m from the roadway edge.

[b] Mean value for measurements of samples taken 85 to 310 m from the roadway edge.

*** Means values differ significantly at $p < 0.001$.

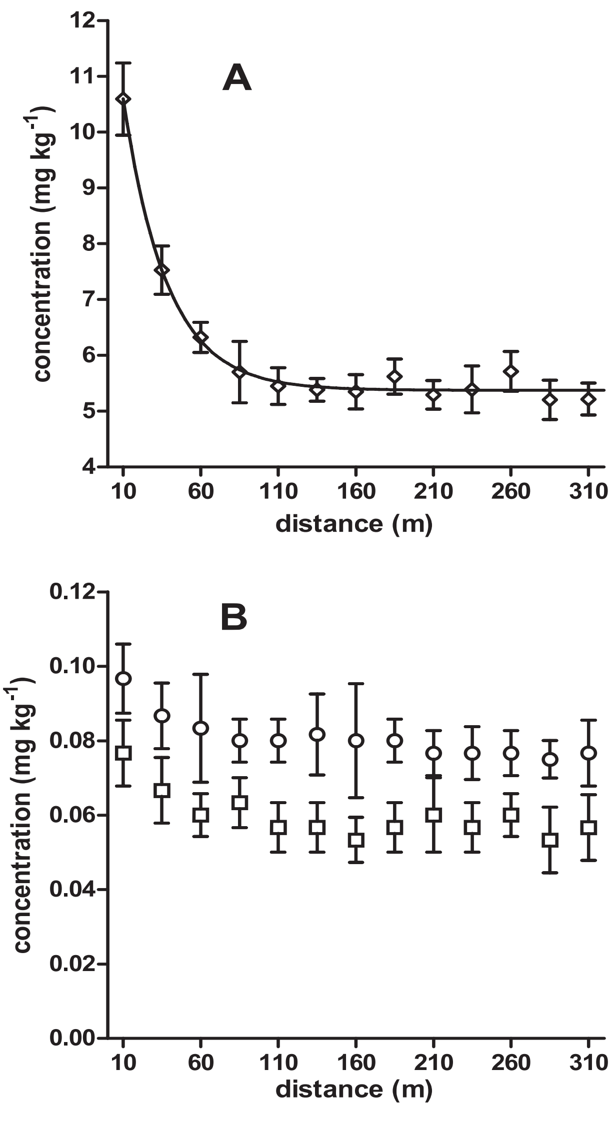

Fig. 1. Dependence of lead content in soil (A), barley grain (B — circles), wheat grain (B — squares) on the distance from the roadway.

kg-1, which means that it was 114- and 84-fold lower respectively than the mean concentration in soil samples. Lead accumulation in grain, compared with its mean soil concentration, was at a level of a thousandth part of the decimal fraction. Similar results concerning lead accumulation in wheat grain were reported by Bojarska and Bzowski [20].

The lead concentrations in cereal grain were relatively low and similar to the levels determined in the Warmia and Mazury region by Sobiech et al. [21]. According to the Regulation by the Minister of Health [22], the calculated mean lead concentration in wheat grain constituted 30%, and in barley grain 40.5%, of its maximum acceptable level. The difference between the mean lead concentrations in wheat and barley grain was statistically significant at $p<0.001$ (Table 2, Fig. 1). The 35% higher lead concentration in barley grain could be caused by a more developed ear surface, adsorbing more airborne particulates, as well as other specific characters [5, 6, 7].

The concentration of cadmium in soil samples was not correlated to the distance from the road, and was generally low — the mean level was 0.015 mg kg^{-1} (Table 2). In uncontaminated arable soils cadmium concentration varied from 0.01 to 0.7 mg kg^{-1}. According to Bem and Turzyńska [23], and Kocjan et al. [24], the natural cadmium concentration in such soils in Poland varies between 0.1 to 1.7 mg kg^{-1}. However, in some soil surface layers investigated by Szymczak et al. [15], the cadmi-

Table 3. Lead and cadmium content (mg kg^{-1}) of wheat, barley and soil in Poland, according to reported literature.

Metal reference	Samples from:	Wheat Range (mean)	Barley Range (mean)	Soil Range (mean)
Lead				
Czarnowska [18]	Urban area (Warsaw) Close to the street			111-366 (184.3)
	100 m from the street			29-110 (64.5)
Czarnowska [11]	Urban area (Łódź) Parks			39-409 (95)
	Suburban area (Łódź)			8-105 (37.5)
Pillich [28]	Area of a planned highway A4 (Łany)			7-122 (45.5)
	Area of a planned highway A1 (Wilków - Lubojenka)			7.48-45.6 (19.1)
	(Piekary – Podmłynie)			70.8-4090 (544.0)
Szymczak *et al*. [15]	south-western Poland Agricultural areas	0.118-0.520 (0.227)	0.16-0.76 (0.267)	3-67.5 (8.0)
Jasiewicz *et al*. [28]	Silesian Province Agricultural areas		0.63-3.14 (1.76)	16.61-70.02 (34.42)
Sobiech *et al*. [21]	Warmia and Mazury Province (Wrócikowo near Olsztyn)	0.03-0.07 (0.05)		
Inspectorate for Environmental Protection [19]	Warmia and Mazury Province (Tomaszkowo near Olsztyn)			11.5[a] 10.5[b]
Cadmium				
Czarnowska [18]	Urban area (Warsaw) Close to the street			1.01-2.97 (2.07)
	100 m from the street			0.12-2.61 (1.05)
Czarnowska [11]	Urban area (Łódź) Parks			0.42-1.66 (1.02)
	Suburban area (Łódź)			8-105 (37,5)
Pillich [27]	Area of a planned highway A4 (Łany)			0.4-0.9 (0.53)
	Area of a planned highway A1 (Wilków - Lubojenka)			0.27-1.03 (0.5)
	(Piekary – Podmłynie)			1.18-187 (26.2)
Szymczak *et al*. [15]	south-western Poland Agricultural areas	0.02-0.172 (0.062)	0.014-0.084 (0.039)	0.0-0.295 (0.116)
Sobiech *et al*. [21]	Warmia and Mazury Province (Wrócikowo near Olsztyn)	0.062-0.128 (0.084)		

[a] Mean value for measurements taken 25 to 50 m from the roadway edge in 1990.

[b] Mean value for measurements taken 25 to 50 m from the roadway edge in 1996.

Table 4 Maximum allowable concentrations of lead and cadmium in soil, wheat and barley in Poland.

Reference	Samples from:		Lead /mg kg^{-1}	Cadmium /mg kg^{-1}
Minister of the Environment [26]	Soil	Protected areas	50	1
		Agricultural areas	100	4
		Industrial areas	200	10
Minister of Agriculture and Rural Development [29]	Soil	Ecological farms	50-100	0.75-1.5
Minister of Health [22]	Wheat		0.2	0.1[a]
	Barley		0.2	0.1

[a] 0.2 mg kg^{-1} — on Poland's accession to the European Union.

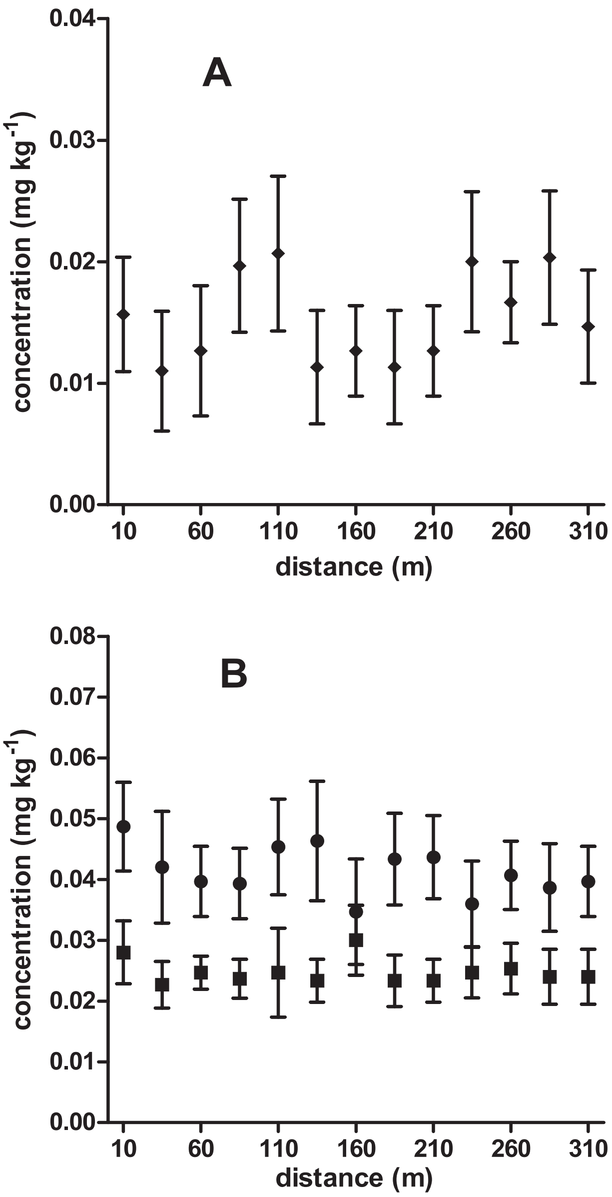

Fig. 2. Dependence of the cadmium content in soil (A), barley grain (B — shadowed circles), wheat grain (B — shadowed squares) on the distance from the roadway.

um content was lower than the detection limit of the method applied (0.001 mg kg^{-1}) (Table 3). The results of soil quality monitoring carried out by the Ministry of Agriculture and Rural Development [14] in 2000 show that the lowest cadmium concentration, about 0.04 mg kg^{-1}, was recorded in northeastern Poland (including Warmia and Mazury) and central Poland [23]. According to the Regulation on Soil Quality Standards of 2002 by the Minister of Environmental Protection [25], the permissible cadmium concentration is much higher, e. g. 1 mg kg^{-1} in protected areas, and 4 mg kg^{-1} in the surface layer of arable soils (Table 4).

The cadmium concentration in cereal grain was in all cases higher than in soil samples (Fig. 2). Similarly, as in the case of soil, it was independent of the distance from the road. The average cadmium content of wheat grain was 0.025 mg kg^{-1}, and of barley grain — 0.041 mg kg^{-1} (64% higher). The difference between mean cadmium concentration in barley and wheat grain was statistically significant at $p<0.001$. Cadmium accumulation in grain, compared with its mean soil concentration, was 1.7 in wheat and 2.7 in barley. The mean cadmium concentration in wheat grain constituted 25%, and in barley grain 41%, of its maximum acceptable level (Table 4).

The results of several studies indicate that cadmium taken up by plants from the soil is accumulated first of all in roots, and then transported in smaller quantities to stems and seeds [7, 21]. Cadmium concentration in other plant organs depends on numerous factors, such as specific characters of the plant species and physicochemical properties of the soil, as well as dust deposition [1, 7]. The grain for analyses was obtained from slightly acid and acid soils (pH 5.1 to 5.8), i. e. conducive to intensive cadmium uptake by plants, despite its very low concentration in arable soils [1, 7, 21].

The results obtained confirm slight accumulation of lead in cereal grain, compared with its concentration in the soil, and higher cadmium accumulation in grain of cereals grown on acid soils. The heavy metal concentrations in grain were affected by cereal species.

A comparison of the results obtained with those reported by other authors (Table 3) shows that the road segment chosen for the experiment had no significant effect on lead and cadmium concentrations in the soil surface layer. The chemical composition of dusts and soils adjacent to roads in big agglomerations and industrial centers indicates a much higher degree of pollution by these elements [18, 26]. The maximum lead and cadmium concentrations determined by the Provincial Inspectorate for Environmental Protection [27] in the city of Katowice in soil samples from the area of a planned highway, A1 (Podmłynie-Piekary Śląskie segment), are comparable only with their concentrations determined in metallurgical industry wastes [28].

Despite considerable lead and cadmium pollution of the soil surface layer close to roads and in industrialized areas (Table 4), in 2000 in Poland only 1% of the samples examined were characterized by increased lead content, and 7% by increased cadmium content [14].

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