

Entry of Heavy Metals into Food Chains: a 20-year Comparison Study in Northern Moravia (Czech Republic)

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Abstract

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The aim of the study presented here was to assess cadmium, lead and mercury contamination of wild-living animals and cattle in Northern Moravia (Czech Republic). Samples were collected in 2005–2007 at the same locations as in 1986–1989, in the same season of the year, and they were analyzed using the same methods (AAS). In 2005–2007, a significant decrease ($P < 0.01$) in cadmium concentrations in plant fodders was found, while changes in lead and mercury concentrations were less marked, and they depended on the type of commodity. In the 2005–2007 period, a marked decrease ($P < 0.01$) in cadmium concentrations in the muscle and kidneys of the cattle, fallow deer, roe deer and pheasants (muscle 0.002–0.009 mg·kg⁻¹, kidneys 0.11–0.69 mg·kg⁻¹) was found. In the same period, mercury concentrations in the muscle, liver and kidneys were significantly lower ($P < 0.01$) in cattle, roe deer and hare tissues (muscle: 0.6–3.5 µg·kg⁻¹, liver 3.3–41.0 µg·kg⁻¹, kidney 16.3–43.2 µg·kg⁻¹). Lower lead concentrations in the 2005–2007 period were only found in cows (0.04 mg·kg⁻¹, 0.1 mg·kg⁻¹ and 0.6 mg·kg⁻¹ in muscle, liver and kidney samples, respectively). No significant differences in lead concentrations were found in the tissues of other animals.

The study demonstrated a reduction in the amounts of heavy metals entering food chains in the study area in recent years.

Cadmium, lead, mercury, muscle, liver, kidney, feedstuffs, AAS

Certain metals are an indispensable part of biomolecules, and one third of enzymes need metal ions for their catalytic activity. On the other hand, some metals have no natural biological function (e.g. cadmium, mercury and lead). When released to ecosystems, these metals accumulate in food chains and their toxic effects disrupt the existing biological balance (Beiglbock et al. 2002; Massanyi et al. 2000ab, 2005; Miadoková et al. 2000). Metals are introduced to ecosystems via natural routes and by anthropogenic processes. The greatest increase in toxic elements in the environment and the agrarian ecosystem was caused by the development of industry in the last century (Jones et al. 1987; Schulte-Rentrop et al. 2005). Beside immissions, the main reasons for increasing metal concentrations in the soil included the use of inorganic fertilizers, herbicides, pesticides and fungicides (Alloway et al. 1990; Mortvedt and Beaton 1995). Accumulation of heavy metals may block biochemical processes in soils and facilitate the entry of toxic metals into food chains (He et al. 2005). At the end of the last century, the entry of heavy metals into food chains was studied by a number of authors (e.g. Andersson and Bingefors 1985; Brams and Anthony 1985), who helped identify and eliminate possible sources of contamination, and monitored the effects on the flora and fauna (Yaaqub et al. 1991; Gnamus et al. 1995, 2000; Toman et al. 2005). These issues remain topical even today.

Northern Moravia (Czech Republic) is an area with marked industrial contamination (Hůnová 2003; Grodzinska 2003) and it came into focus when the issue of safe food production in an industrially contaminated area was studied in the 1980s (Zima et al. 1990).

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The aim of the present study was to determine present-day concentrations of cadmium, lead and mercury in selected plant materials from the same locality, and to compare heavy metal concentrations in cattle and wild animals with the situation of 20 years ago using the same analytical methods.

Materials and Methods

The studies were made in Northern Moravia (Czech Republic) on the Nový Jičín farm of the University of Veterinary and Pharmaceutical Sciences Brno in 1986–1989 and in 2005–2007 (Fig. 1). The research area included a game enclosure, i.e. a fenced-in area of 250 ha for the breeding of hoofed game (marked as 1 and 2) and a hunting ground of 1,400 ha of agricultural land that included arable land (Nos 4, 5, 6 and 9) and meadows and pastures (Nos 3, 7 and 8). Samples of soil, water, mineral fertilizers, plants and tissues of wild animals were taken at those sites. At animal production premises, samples of milk, animal feeds, supplementary feeds, drinking water and samples of tissues of slaughtered cows were taken. Between 1986 and 1989, over 1,200 samples were tested for cadmium, lead and mercury contamination. In 2005–2007 we analyzed 239 samples. Our study focussed specifically on those areas where elevated concentrations of the elements monitored were recorded. Samples were always collected at the following three intervals: I - first decade in May, II - third decade in July, III - first decade in October.

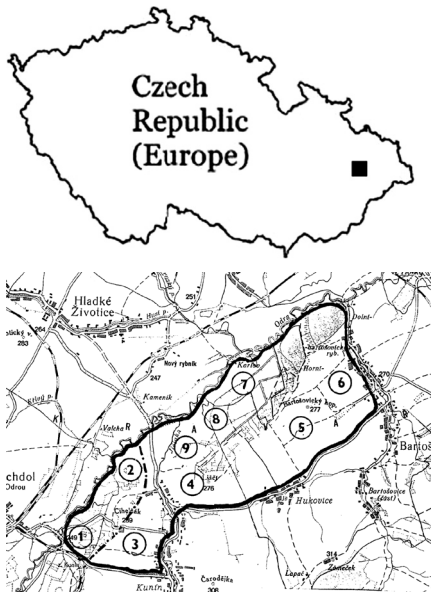


Fig. 1. Location of the research area (1, 2 - deer-forest; 4, 5, 6 and 9 - arable land; 3, 7 and 8 - meadows and pastures).

Soil

Soil samples were leached in hot nitric acid (2 mol·l⁻¹). The leachates obtained were analyzed for the presence of Cd and Pb using flame AAS (Z-5000 spectrometer, Perkin Elmer, USA).

Mercury determination in all samples was performed on single-purpose mercury analyzers TMA-254 (detection limit 1 ng) and, in the 2005–2007 study, AMA-254 (detection limit 0.01 ng) manufactured by Altec s.r.o., (CR).

Tissues

Prior to Cd and Pb determination, dried-up samples of plant tissues and native samples of animal tissues (1 g) were mineralized in laboratory autoclaves using nitric acid. In the 1980s traditional heating in the drying chamber was used. In the present study microwave heating was used instead (Ethos Sel, Milestone, Italy). Both in the 1980s and today, cadmium and lead were determined using atomic absorption spectrometry (AAS) with electrothermal atomization by a Z-5000 (Perkin Elmer, USA). Detection limits (3σ) for cadmium and lead in tissues were 1.25 μg·kg⁻¹ and 10 μg·kg⁻¹, respectively. In all cases, the procedures were verified using standard reference materials, specifically H-9 and V-10 (IAEA Vienna), 1577a NBS (USA) Nos 184, 185 and 186 (CRM Belgium) and Lucerne P-ALFALFA (Czechoslovak Metrologic Institute).

UNISTAT 5.1. software was used to statistically evaluate the metal concentrations found.

Results and Discussion

Soil

The selected study sites are characterized by the predominance of loamy to clayey soils. In 1986–1989, a total of 126 soil samples were examined. The ranges of cadmium, mercury and lead concentrations in soil were 0.29–0.6 mg·kg⁻¹, 0.31–2.14 mg·kg⁻¹ and 17–31 mg·kg⁻¹, respectively. The analysis of mineral fertilizers used in 1986–1989 and of immission records from that period indicated a heavy contamination of the monitored countryside with hazardous metals, aggravated by acid precipitations (pH = 4.9–5.6 and Hg 0.4–1.0 μg·l⁻¹, Pb 9–29 μg·l⁻¹ and Cd 8–14 μg·l⁻¹) (Zima et al. 1990).

In the present study, 20 soil samples were analyzed. A significant increase ($P < 0.01$) in soil cadmium concentrations (1986–1989: 0.32 ± 0.10 ; 2005–2007: 0.88 ± 0.24 mg·kg⁻¹) at sites 1 and 2 (game enclosure) was found. Most of the game enclosure area is not

agriculturally managed land. It is an inundation area of the Odra river, and its floodwater and especially its sediments may account for the higher cadmium concentrations in the game enclosure soil. In the game enclosure area, a significant ($P < 0.05$) increase in soil pH ($6.1 \pm 0.2 \rightarrow 6.7 \pm 0.3$) was found as a result of intensive liming of the inundation area. There was only a small non-significant increase in pH at the remaining part of the area monitored (6.4 ± 0.3), with no significant differences in soil concentrations of the tested substances in individual time periods, which is in good agreement with literary data (Bergkvist et al. 2003; Makela-Kurtto and Sippola 2002; Wang et al. 1997).

Feedstuffs

Cadmium is an element with a high bioaccumulation index in the 1–10 range (Pais and Jones 1997). Cadmium concentrations (Fig. 2) in plant feedstuffs from individual sites in the 1980s were significantly higher ($P < 0.01$), except for wheat shoots ($P < 0.05$), compared with the 2005–2007 period. Cadmium concentrations in plants depend on the plant species and the growth stage, and it is in correlation with cadmium concentration in the soil and the soil pH, because high soil pH levels reduce cadmium availability for plants (Jones and Johnston 1989). This trend was particularly noticeable in the game reserve (1, 2).

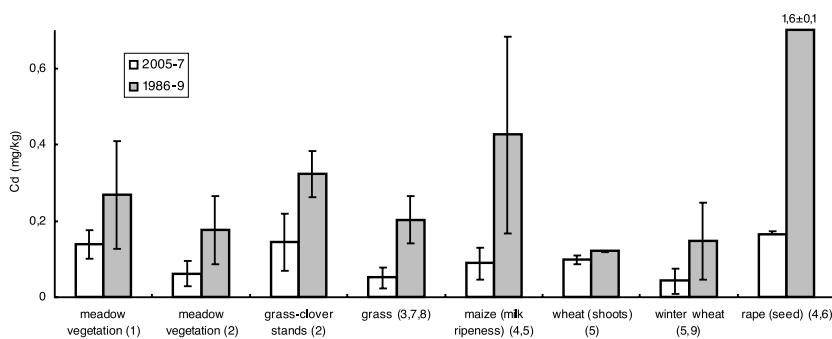


Fig. 2. Cadmium concentrations in plant feedstuffs (mean \pm SD)

Bioaccumulation index of lead is quite low (0.01–0.1), and its entry into food chains depends largely on anthropogenic activities (Pais and Jones 1997). Although the amounts of lead released into the atmosphere have been reduced in recent decades (Harmens et al. 2004; Schulte-Rentrop et al. 2005), lead concentrations in meadow vegetations showed no significant decrease in 2005–2007, contrary to farm crops ($P < 0.05$) (Fig. 3). This may be due to the accumulation of lead in the topsoil of land with perennial stands.

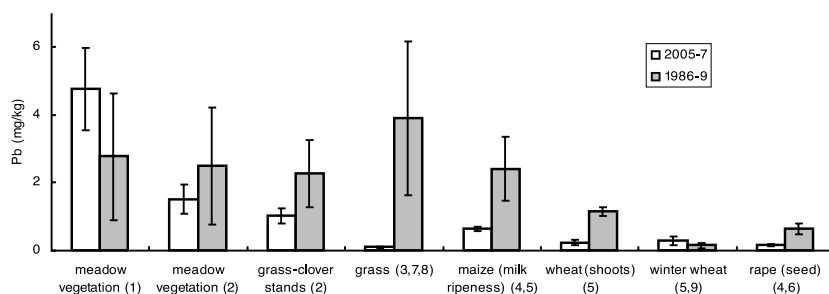


Fig. 3. Lead concentrations in plant feedstuffs (mean \pm SD)

In contrast to cadmium and lead concentrations, mercury concentrations in plant material (Fig. 4) showed no significant changes. A significant decrease in mercury concentrations was found only in winter wheat grain and oilseed rape seed. A slight increase, on the other hand, was found in meadow vegetation in the game enclosure. The mercury cycle is responsible for the steady state or even increasing levels of mercury in the environment (Dastoor and Larocque 2004; Houserová et al. 2006; Ryaboshapko et al. 2007).

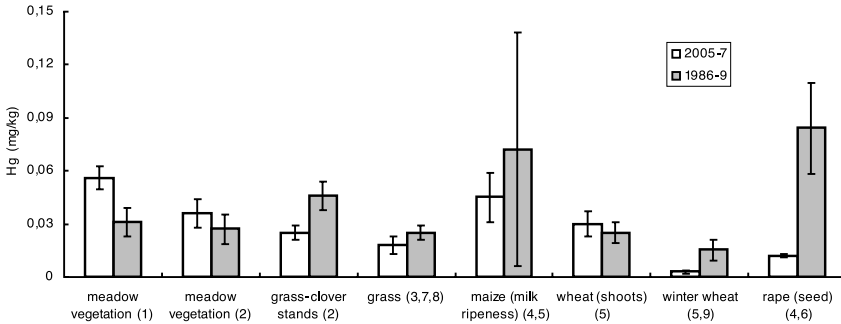


Fig. 4. Mercury concentrations in plant feedstuffs (mean ± SD)

Animal tissues

Cadmium, lead and mercury concentrations in tissues of cows and wild animals are presented in Table 1. The age of wild animals from the 1986–1989 study was not accurately determined. All the animals were, however, at the age when they are usually harvested.

Cadmium

In both cows and wild animals, a significant ($P < 0.01$) decrease in cadmium concentrations compared with the 1986–1989 study was found in muscle tissues only. This is suggestive of lower cadmium intake levels at which the organism is still able to detoxicate and excrete the element rather than storing it in muscle tissue (Györi et al. 2005; Neathery et al. 1974). In both periods, cadmium concentrations in kidneys were higher ($P < 0.01$) than those in the muscle and liver ($P < 0.05$), and they are in good agreement with literature data (Gašparik et al. 2004). In hares, cadmium concentrations in the liver and kidneys were higher in the 2005–2007 period. That finding, however, is not relevant in view of the small number of samples examined in that period.

Lead

A significant decrease ($P < 0.01$) in lead concentrations in the muscle, liver and kidneys was found in cows. In wild animals, however, the trend was not significant, which was in line with levels found in meadow vegetation. Higher concentrations ($P < 0.05$) were found in the kidneys. In recent years, an increase has been recorded in drakes, but the results are not relevant because of the low number of samples examined.

Mercury

A significant decrease ($P < 0.01$) in concentrations of mercury in all the tissues examined (except for drakes) was found in comparison with the 1986–1989 study. In all the animals, mercury concentrations in kidneys were higher ($P < 0.05$) than mercury concentrations in muscle tissues in both monitoring periods.

Beside feedstuffs, drinking water was also examined. Concentrations of cadmium, lead and mercury in all water samples were very low and met the drinking water standards. Metal concentrations in milk were also below metal detection limits in both monitoring periods.

Table 1. Concentrations of cadmium, lead and mercury in animal tissues

Animal	Tissue	Year	n	Age (years)	Cd (mg·kg ⁻¹) mean ± SD	Pb (mg·kg ⁻¹) mean ± SD	Hg (μg·kg ⁻¹) mean ± SD
Cows	muscle	2005-7	6	3-4	0.004 ± 0.001	0.041 ± 0.016	1.1 ± 1.0
		1986-9	6	3-4	0.050 ± 0.023	0.253 ± 0.039	21.0 ± 5.1
	liver	2005-7	6		0.095 ± 0.029	0.059 ± 0.014	3.3 ± 0.7
		1986-9	6		0.084 ± 0.016	0.586 ± 0.111	24.3 ± 4.5
	kidneys	2005-7	6		0.612 ± 0.134	0.072 ± 0.030	18.3 ± 2.3
		1986-9	6		0.728 ± 0.204	0.291 ± 0.066	51.0 ± 9.4
Fallow deer	muscle	2005-7	25	3.3 ± 1.8	0.006 ± 0.004	0.079 ± 0.104	0.6 ± 0.3
		1986-9	3	3-4	0.032 ± 0.011	0.095 ± 0.062	
	liver	2005-7	25		0.069 ± 0.152	0.198 ± 0.203	3.0 ± 2.2
		1986-9	3		0.120 ± 0.031	0.392 ± 0.217	
	kidneys	2005-7	25		0.692 ± 0.470	0.124 ± 0.172	27.0 ± 24.0
		1986-9	3		0.655 ± 0.302	0.214 ± 0.016	
Roe deer	muscle	2005-7	7	2.7 ± 0.2	0.007 ± 0.002	0.099 ± 0.022	0.6 ± 0.2
		1986-9	14	3-4	0.045 ± 0.038	0.070 ± 0.062	11.1 ± 6.7
	liver	2005-7	7		0.221 ± 0.226	0.060 ± 0.033	1.5 ± 0.6
		1986-9	14		0.278 ± 0.141	0.448 ± 0.177	5.0 ± 2.0
	kidneys	2005-7	7		0.685 ± 0.246	0.160 ± 0.159	16.3 ± 7.2
		1986-9	14		1.730 ± 1.695	0.308 ± 0.258	136.4 ± 4.6
Drakes	muscle	2005-7	2	3-4	0.009 ± 0.006	0.140 ± 0.077	89.3 ± 78.2
		1986-9	8	3-4	0.020 ± 0.006	0.028 ± 0.009	27.5 ± 15.0
Pheasants	muscle	2005-7	10	2-3	0.003 ± 0.001	0.029 ± 0.027	1.5 ± 0.9
		1986-9	23	2-3	0.023 ± 0.016	0.050 ± 0.012	9.1 ± 8.2
	liver	2005-7	10		0.033 ± 0.008	0.150 ± 0.062	6.2 ± 4.4
		2005-7	10		0.110 ± 0.032	1.204 ± 0.182	22.8 ± 13.1
Hares	muscle	2005-7	2	2-4	0.002 ± 0.001	0.016 ± 0.011	3.5 ± 0.5
		1986-9	10	2-4	0.020 ± 0.008	0.034 ± 0.019	12.8 ± 9.1
	liver	2005-7	2		0.562 ± 0.039	0.092 ± 0.015	41.0 ± 4.1
		1986-9	5		0.147 ± 0.072	0.284 ± 0.083	347 ± 200
	kidneys	2005-7	2		8.84 ± 2.00	0.121 ± 0.023	43.2 ± 4.2
		1986-9	5		2.07 ± 0.26	0.204 ± 0.094	1466 ± 319

Concentrations of cadmium, lead and mercury in hooved game found in 1986–1989 are in agreement with values found in 1987–1991 in Poland (Falandysz 1994). Preferential food items in the wild animals' diet may include plant species that have greater toxic metal accumulation capability, which may account for higher concentrations of those metals in some species of wild animals. Those species reflect the situation in the environment and are used as bioindicators (Gnamus et al. 2000; Kierdorf H and Kierdorf U 2000; Kottferová and Koréneková 2000; Frolich et al. 2001). Waterfowl migration over large areas and their feeding habits give a picture of the overall quality of the environment (Snively and Flaspohler 2006).

Mobility and bioavailability of metals is governed by a number of chemical and biochemical reactions, e.g. precipitation - solubility, adsorption - desorption, oxidation - reduction and dissociation - complexation (Mortvedt and Beaton 1995; Wenzel et al.

1999). Mobility of elements is also greatly affected by soil extract pH (Tlustoš et al. 1995; Öborn et al. 1995). An increasing pH greatly reduces the mobility of Cd and, partially also of Pb. Although there was no demonstrable change in soil pH in the study area (with the exception of the game reserve), there was a reduction in the amounts of toxic metals entering the food chain. Another factor is the concentration of elements in individual layers of the soil. In uncultivated land, complex-forming elements remain in upper layers and metal concentrations on the surface increase due to immissions (He et al. 2005; Sichorová et al. 2004).

Concentrations of cadmium, lead and mercury found in animal tissue samples taken in 2005–2007 are low and represent no health risk for consumers. The findings reflect improvements in the quality of the environment not limited only to the Czech Republic (Hůnová 2003; Wang 1997), and also the integration of research results in agricultural practice. The result is a decreasing trend of risk elements entry into the food chain.

Vstup těžkých kovů do potravních řetězců: porovnání po 20 letech na území severní Moravy

Cílem předkládané práce bylo posouzení zátěže (kontaminace) volně žijící zvěře a skotu kadmíem, olovem a rtuťí na území severní Moravy. Vzorky byly sbírány v letech 2005–2007 na stejných lokalitách jako v roce 1986–1989, ve stejném ročním období a analyzovány shodnými metodami (AAS). V letech 2005–2007 bylo zjištěno statisticky průkazné snížení ($P < 0,01$) obsahu kadmia v rostlinných krmivech, změna u olova a rtuťí nebyla tak výrazná a byla odvislá od druhu komodity. Výrazné snížení ($P < 0,01$) koncentrace kadmia ve svalovině a ledvinách bylo zjištěno u skotu, daňků, srnců a bažantů v letech 2005–2007 (svalovina 0,002–0,009 mg·kg⁻¹, ledviny 0,11–0,69 mg·kg⁻¹). Koncentrace rtuťí ve svalovině, játrech a ledvinách byla signifikantně nižší ($P < 0,01$) u tkání skotu, srnců a zajíců v letech 2005–2007 (svalovina: 0,6–3,5 μg·kg⁻¹, játra 3,3–41,0 μg·kg⁻¹, ledviny 16,3–43,2 μg·kg⁻¹). Snížené koncentrace olova ve tkáních v období 2005–2007 bylo zjištěno pouze u krav (svalovina 0,04, játra 0,1 a ledviny 0,6 mg·kg⁻¹), tkáně ostatních zvířat nevykazovaly signifikantní změny.

Výzkum prokázal snížený vstup těžkých kovů do potravních řetězců na sledovaném území v posledních letech.

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