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Heavy Metals in Falling Dust in Eastern Mazowieckie Province

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Abstract

Deposition of Cu, Zn, Mn, Cr, Ni, Pb and Cd, and their concentrations in falling dust were measured in 1995-1998 in eastern Mazowieckie Province (former Siedleckie Province). No maximum permissible values of dust deposition, nor Pb and Cd concentrations, were exceeded. It was observed that the elements of low melting temperatures (Pb, Zn) reached higher concentrations in paniculate matter, and higher deposition level in heating season compared with summer. Among all the examined metals Ni appeared to be the most stable in falling particulate matter. The results indicate that the main source of metals in falling particulate matter is the thermal and electric power industry.

Keywords: Mazowieckie Province, heavy metals, dust deposition, power plant, atmospheric pollution

Introduction

The particulate and gaseous pollutants emitted into the atmosphere cause a serious threat due to their quick and uncontrolled spread. They also directly and adversely affect living organisms. In Poland, fossil fuels and the power industry, especially coal combustion, are chief sources of heavy metals in the atmosphere. About 70% of electric power plants in Poland are fueled by coal [1]. It is estimated that approximately 70% to 94% of total heavy metal emission into the atmosphere results from fossil fuel use by the power industry. In the entire pool of heavy metal emission into the atmosphere discharge from individual family households, and from the local municipal coal-fired boiler plants [2, 3] predominate. Being not equipped with dust-arresting facilities (particulate control) and being low emitters, on a country's scale they constitute numerous dissipated sources. Dust is the carrier of heavy metals in the atmosphere from which they get into the soil. The network of the atmosphere monitoring stations measure deposition of Cd and Pb [4, 5]. When evaluating the level of heavy metal pollution in soil alongside Pb and Cd, also Ni, Cu, and Zn are considered [6]. According to the Polish Legislature, no maximum permissible levels of these metals in dust deposits have been set. The level on heavy metal pollution may be evaluated from the level of dust deposition per unit area and metal concentration in the deposit. Such an evaluation should be carried out not only in industrial areas but also, due to dispersion of heavy metal sources, in agricultural ones.

Over the last 20 years atmospheric metal emission in Poland considerably decreased. According to statistical data, emission values of metals in 1980 and 1997 were: Pb - 2453.9 and 895.8 tons, Cd - 156.2 and 85.5 tons, Cu - 1971.1 and 475.1 tons, Zn - 5387.1 and 2579. 6 tons, Ni - 571.7 and 364.9 tons, respectively [1]. This undoubtedly resulted from the liquidation of many factories in Poland, and a decrease of industrial production. At present, power plants are the main source of environmental con tamination with heavy metals.

The aim of the following work was to estimate the level of dust deposition of Cn, Zn, Fe, Mn, Cr, Ni, Pb and Cd. An evaluation of their concentration in dust deposit in eastern Mazowieckie Province (mainly within the administrative borders of the former Siedleckie Province) was performed.

Studys and Methods

Research was conducted in the eastern region of Mazowieckie Province, which comprises the area of the former Province of Siedlce (Fig. 1). The examination covered the area of the three cities: Siedlce, Mińsk-Mazowiecki, and Sokoiow Podlaski along with six commune localities (Jabłonna Lacka, Maciejowice, Miastków Kościelny, Repki, Trojanow, Zelechow), situated in the south-west and north-east part of the former Siedlce Province. A total number of 12 sites covering the area of 2000 km^2 were sampled. The study lasted from 1995 through 1998. The samples were collected on a monthly or quarterly basis, and each site was sampled for at least one year. Dust samples collected into developing trays of 0.1 mr. This method of sampling is reccomendcd to determine the size of radioactive radionuclides [7]. To avoid sample deposits being blown away by the wind, the trays were covered with a thin layer of vaseline. The deposit was collected with rain water. After the water was evaporated, the dry deposit was mineralized in a combustion furnace at 420°C for 24 hours. The mineralized samples were weighed, then dissolved in a concentrated nitric acid and in hydrogen peroxide. The samples of sediment of < 0.5 g were dissolved in 2 cm^3 of nitric acid and 1 cm^3 of hydrogen peroxide, and transferred to the volumetric flasks of 25 cm^3. The samples of > 0.5 g were dissolved in 4 cm^3 of concentrated nitric acid and 2 cm^3 of hydrogen peroxide, then transferred into the flasks of 50 cm^3. The sediment samples were washed on the filter with hot nitric acid (10 and 20 cm^3, respectively), and filled with doubly distilled water.

Concentrations of metals were measured using AAS (Carl Zeiss Jena AAS 30), with acetylene-air flame. In case of low content of cadmium and lead in the analyzed samples, this element was determined *via* excitation in a graphite tray. Measurements in the graphite tray were done applying background correction under the following conditions: for cadmium - incineration temperature 250°C, atomization temperature 1200°C, concentration range of standard solutions 0.001-0.006 μg/cm^3, for lead - incineration temperature 500°C, atomization tempera-, ture 1400°C, concentration range of standard solutions

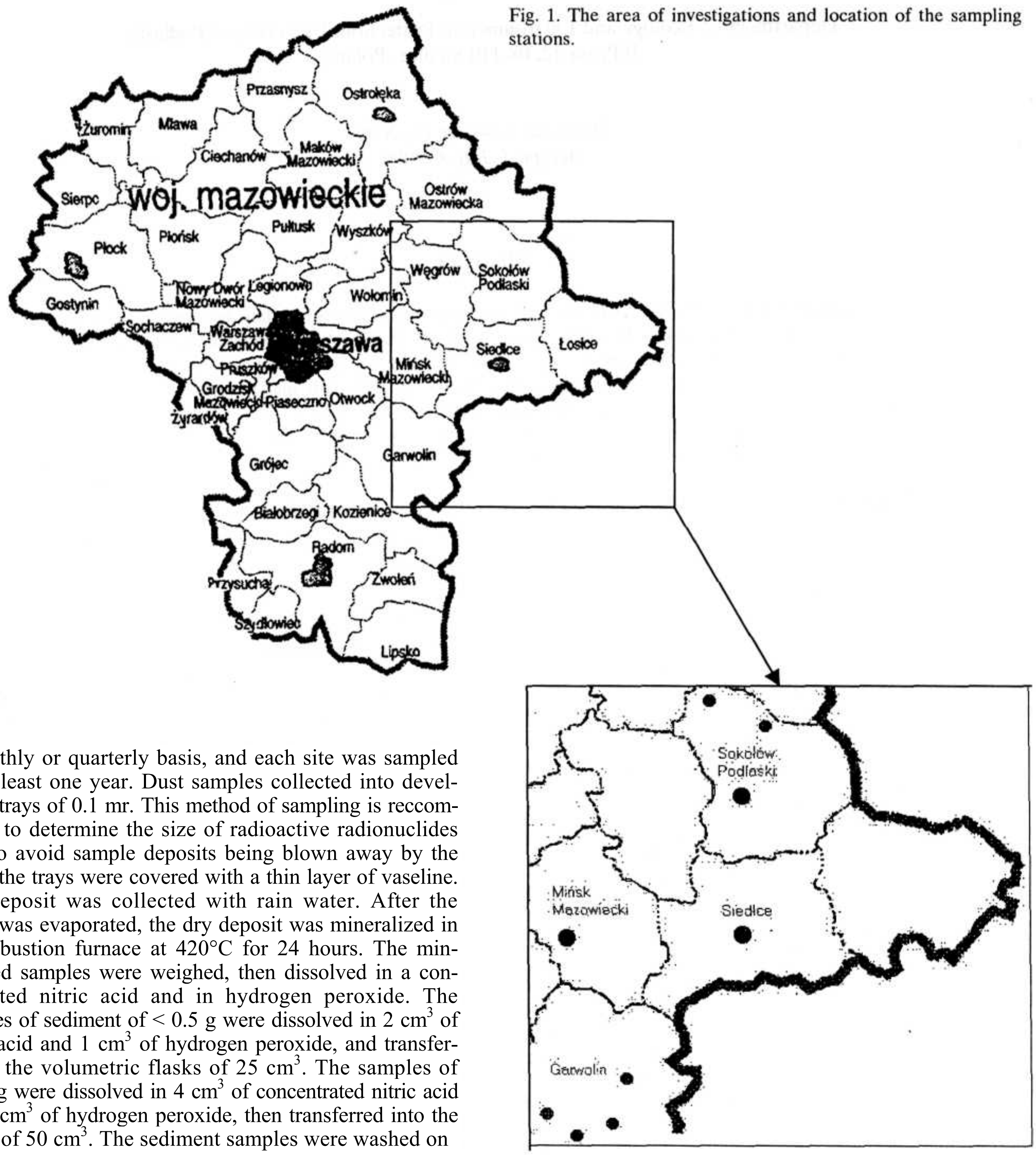

Fig. 1. The area of investigations and location of the sampling stations.

0.01-0.06 μg/cm^3. Other metals were analyzed in flame, at the length of furnace slit 1 = 10 cm, and within the range of standard solution concentrations (μg/cm^3) of: Cu - 0.1-2 and 2-20, Zn - 0.4-6.4, and 6-50, Mn - 0.3-6 and 6-40, Fe - 1.2-20, 20-100 and 100-300, Ni - 0.1-1.0, Cr - 0.1-1.0, Pb - 0.5-3, Cd - 0.1-3. If concentrations of metals in the samples exceeded these ranges, the sol utions were diluted. Reagent blank was used to calibrate the apparatus.

Daily dust deposition, daily deposition of each metal, and their concentration in the dust were calculated from the results of AAS measurements, deposition time and area, and mineralized dust weight.

Average dust deposition, average load of each metal, and metal concentration in the deposit were also calculated for summer samples (April - September), and for heating season (October - March). In addition, the mean dust and metal deposition was estimated for 1 km^2, throughout the whole period of research, alongside the mean concentrations of the metals in the deposit.

The results were statistically analyzed using Statistica package [8].

Results and Discussion

Over the entire study period (1995-1998) mean yearly deposition of metals ranged from several to hundreds of kilograms per 1 km^2. The lowest mean yearly deposition was observed for Cd - 0.66 kg/km^2, Cr- 2.62 kg/km^2, and Ni - 3.25, while the deposition of Cu, Mn, Pb, was higher - 20.4; 41.5; 47.8 kg/km^2, respectively. In the same period, mean yearly dustfall per 1 km^2 of the surface reached 86.9 tons.

Metal deposition, except iron, was higher in heating season (fall and winter) compared to summer. Particularly high differences were observed for zinc and lead. Mean daily deposition of Zn reached 660.3 μg/m^2 in summer, almost twice as much in winter - 1278.8 μg/m^2 (Table 1). For lead the values of 98.9 μg/m^2 and 164.7 μg/m^2 were noted, respectively. Mean dust deposition was, however, slightly higher in summer than in winter - 248.2 and 227.5 mg/m^2 per day.

Concentrations of Zn, Ni, Cr, and Pb in the dust were higher in winter than in summer. Highest differences were observed, similarly as in metal deposition, for Pb and Zn. Mean concentration of Pb in winter dust deposit was 1.5 fold higher than in summer (688.8 mg/kg and 470.9 mg/kg, respectively). Zinc concentration was about 1.8 times higher in winter compared to summer and was reported to be 5772.4 and 3183.3 mg/kg, respectively. In the entire time of research the following quantities of metals were calculated (mg/kg): Cu-521.6; Zn-4443.3; Mn-392.3; Ni-40.0; Fe-17702.8; Cr-29.4; Cd-10.8; Pb-576.9.

The values of daily deposition of dust, metals and concentrations of metals in dust varied within wide ranges (Table 1). That variation resulted from diversity of the samples collected from various sources.

No permissible values of dust, lead or cadmium

Table 1. The deposition of heavy metals, falling dust and the concentration of heavy metals in falling dust in the eastern areas of Mazowieckie Province.

	Daily deposition [μg/m^2] min – **mean** – max median			Concentration of elements in falling dust [mg/kg]		
element	Summer N = 83	Winter N = 80	Mean yearly deposition [kg/km^2]	Summer N = 83 min – **mean** – max median	Winter N = 80 min – **mean** – max median	mean value
Cu	2.1 – **49.9** – 1199.9 40.2	2.7 – **62.1** – 265.3 53.3	20.4	9.9 – **713.4** – 3369.5 502.4	29.4 – **319.4** – 8228.8 273.7	521.6
Zn	37.7 – **660.3** – 4934.1 516.1	91.8 – **1278.8** – 6796.1 1263.2	350.9	89.7 – **3183.3** – 33878.3 2818.0	321.1 – **5772.4** – 63077.8 3232.4	4443.3
Mn	6.9 – **93.1** – 429.3 80.0	4.9 – **135.3** – 505.1 112.1	41.5	27.8 – **397.2** – 1030.7 361.7	58.2 – **387.1** – 915.3 324.2	392.3
Fe	197.0 – **5590.0** – 28400.0 4389.0	219.0 – **4142.1** – 19000.0 3930.0	840.5	380.0 – **20283.0** – 129300.0 17580.0	3700.0 – **14981.2** – 56250.0 11460.0	17702.8
Ni	0.7 – **8.8** – 29.9 8.2	0.5 – **9.0** – 26.5 8.4	3.25	6.9 – **36.1** – 131.1 32.4	7.4 – **44.1** – 356.1 42.5	40.0
Cr	0.5 – **6.9** – 42.1 5.9	0.7 – **7.5** – 40.5 6.2	2.62	0.8 – **26.5** – 201.9 23.9	1.5 – **32.5** – 196.9 25.1	29.5
Cd	0.2 – **1.73** – 13.9 1.10	0.2 – **1.88** – 13.9 1.4	0.66	0.1 – **12.5** – 83.9 10.5	0.7 – **9.1** – 83.9 7.7	10.8
Pb	2.5 – **98.9** – 528.6 79.2	7.0 – **164.7** – 413.5 156.9	47.8	12.8 – **470.9** – 2614.0 443.8	103.0 – **688.8** – 13831.1 547.6	576.9
dust [mg/m^2]	17.9 – **248.2** – 1303.7 230.7	29.1 – **227.5** – 2882.9 195.8	86916			

deposition were exceeded [4, 5], The mean yearly dust deposition being 86.9 ton/km^2 (86.9 g/m^2) was lower than 200 g/m^2 per year, and similarly, mean Pb deposition equal to 47.8 mg/m^2 and Cd equal to 0.66 mg/m^2 did not surpass the values of 100 and 10 mg/m^2 per year.

The results of measurements of metal content in dust deposition, daily deposition of each metal, and dust were subjected to statistical analysis. The correlation coefficients for the values measured in winter and summer periods are given in Table 2. According to these data, more statistically significant relations occured for the samples taken in summer (40 relationships) than in winter (25 relationships).

A smaller number of statistically significant correlations among dustfall deposition, the deposition of individual metals and their concentration in dustfall in winter indicates various dissipated sources of airborne metals. Among all analyzed metals, the highest number of statistically significant relationships was found for Ni. This element seems to be the most stable among all the determined metals in the dust deposit.

The results of heavy metal determination in dust deposition in the agricultural areas indicate that the power industry contributes to heavy metal pollution of soil. Among the analyzed elements, considerably higher content of Pb and Zn were observed in winter than in summer. These metals, and cadmium, have the lowest melting points (Pb - 327.4, Zn - 419.5, and Cd 320.9°C). Melting points of remaining metals are above 1000°C [9]. So, the elements of the lowest melting points showed the highest emission rates, which have already been mentioned by Hławiczka [2]. According to this author's calculations, the highest emission from individual domestic fires reaches the following values: lead - 14.75 g/Mg carbon and zinc - 59.5 g/Mg. The results obtained in the present work, and the data of other authors [10, 11], show that the processes of total and partial evaporation are signifcant factors affecting the level of their emission. Thermal processes foster emission of more volatile metals of lower melting point.

The data in Table 1 show exceptionally high deposition of Fe and Zn (hundreds of kg per 1 km^2), and their high concentrations in dust (thousands of mg/kg). Higher Fe deposition and its concentration in dust in summer indicate that re-dusting of wind-driven soil particles may be the source of Fe. This is confirmed by correlation coefficients between dust-deposition and the deposition of iron ($r = 0.3273$, $p < 0.01$, $n = 83$; r - correlation coefficient, p - significance level, n - number of samples), as well as between iron and manganese deposition (r ss 0.4434; $p < 0.01$, $n = 83$). Iron and manganese are main soil components. High Zn deposition and its high concentration in dust in areas not exposed to high industrial emissions point to the fact that constant monitoring of this element in dust deposits is necessary. Considering that Zn is taken into account in evaluating heavy metal pollution levels [6], it is vital that Zn deposition standards be introduced.

Higher lead emissions in winter than in summer in the examined areas are in contradiction to the prevailing opinion that exhaust fumes are the main source of lead pollution. The results of the present study confirmed calculations obtained by, among others, Hlawiczka [3]. The author estimated that in 1980-1995 lead emission

Table 2. Correlation coefficients between values: concentration of heavy metals in falling dust (A), daily deposition of metals and dust (B) in eastern areas of Mazowieckie Province in summer and winter.

		dust	Cu		Zn		Mn		Ni		Fe		Cr		Cd		Pb	
		B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
dust	B	X					-0.5040		-0.2450	0.4952		0.3273		0.3648			-0.2296	
Cu	A		X	0.5855					0.3139		0.3683		0.2973					
	B			X					0.3083				0.2418					
Zn	A				X	0.9037												
	B				0.4450	X												
Mn	A	-0.4516					X		0.4912	0.2258								
	B			0.9759				X		0.4202		0.4434		0.3802				0.4020
Ni	A								X	0.4834	0.2704		0.7817	0.5484			0.2443	
	B								0.3247	X		0.2953	0.3697	0.7642				0.2805
Fe	A						0.3885			0.3705	X	0.8210	0.3479	0.2442			0.6532	0.7378
	B				-0.2390					0.5214	0.7011	X		0.3262			0.4965	0.8896
Cr	A						0.2777		0.4977	0.6086	0.2618		X	0.7292				
	B								0.2452	0.8059	0.3703	0.4613	0.8357	X				0.3192
Cd	A						0.3462			0.3336					X	0.9619		
	B						0.3262			0.3336					0.9971	X		
Pb	A		0.2380														X	0.6696
	B																0.9492	

▭ summer ▭ winter

Table 3. Average annual metal deposition in other regions of Poland and Europe.

	Deposition [kg/km² · year]								
	dust	Pb	Cd	Cu	Zn	Mn	Fe	Cr	Ni
Poland:									
Mean for Poland (1997) [15]	88000	31	1.4						
Warsaw-Province (1997) [15]	114000	236	4.7						
Kato Katowice-Province (1997) [15]	68000	38	1.8						
In this:									
Nowy Bytom (1996) [16]		116-170	2.02-4.81	14-68	346-1079	406-1607	25.8-43.6	6.5-16.2	9.6-15.4
Lublin [14]		81		84.5	564	235		16.5	17
Wisła – Health-Resort (1990) [12]		6		1.31	1.5	4.0		2.1	1.64
Coast of the Baltic Sea (only wet deposition) (1997) [13]		0.82	0.76	0.97	5.27				
Europe:									
Germany – Karlsruhe (1992/93 – 1993) [20]		4.0	0.106	3.5					
France – The Arcachon Lagoon (1994-1996) (only wet deposition) [21]		3.4	0.07	1.4	14.4				1.1
Lituania (1993-1995) [22]		2.09	0.086	3.6	9.61	7.1	33.5	0.295	1.03

from fossil fuel combustion constituted 36% of the whole country's Pb load, while from motor vehicles only 27%.

The results of the present study are particularly interesting when compared with results obtained in other cites in Poland and Europe (Table 3). In the former Siedlce Province higher deposition of Cu, Zn, Cr and Ni was noted, compared to Beskid Slaski (Health Resort Wisla) [12], and the amount of wet deposit carried to the Baltic Sea [13]. The deposition of Cd, Zn, Cu and Ni was, however, lower than in Lublin [14] or Silesia [15,16]. Average lead deposition in the former Siedlce Province in 1995-98 exceeded mean values for Poland in 1997 [15]. In 1997 highest lead deposition in Poland was observed in Warsaw Province [15] neighboring Siedlce to the east. Taking into consideration air circulation, and the prevalence of western and south-western winds [17], it is possible that Warsaw Province might have contributed to the pollution of the region under study. That was stressed by Hryniewicz and Przybylska [18] who reported that north-eastern regions of Poland are contaminated by pollutants blown from the south-east.

Deposition of Cd, Pb and Cu observed to the east of Mazowsze Province in 1995-98 was up to several times higher compared to the load of these metals in Germany (Karlsruhe) in 1992-93 [20], in France (The Arcachon Lagoon) in 1994-96 [21], or in Lithuania in 1993-95 [22]. Also deposition of other metals: Zn, Ni, Mn, Fe, and Cr in Lithuania [22] was considerably lower compared to the values noted in the area under study. In Lithuania and France high portions of electric energy are produced by nuclear power plants. The results obtained in the present work confirm that coal combustion is the main source of metal deposition in eastern Poland. Fine dust particles stay long in the air [19], and they are particularly rich in heavy metals [11].

The results of the present work show that Ni, being most stable in dust deposits, can be used as a reference element in calculations of enrichment coefficients of dust with heavy metals. According to Kabata-Pendias and Pendias [23], manganese or aluminum may also be used as reference metals. Taking into consideration the high stability of Ni measurements, statistically significant correlations between the concentration and deposition of Ni and the other metals, as well as low differences of its concentration in the dust and deposition between heating season and summer, it seems that Ni may be applied as a reference element as these results show. It is a proposition for this Mazowieckie Province region.

Conclusions

1. In eastern Mazowsze Province (former Siedlce province) no permissible values of dust, lead or cadmium deposition were exceeded.

2. Higher Zn and Pb deposition, as well as their in creased concentrations in dust deposit in the heating sea son compared with summer, indicate that heating and power plants are the main source of metals in the air. Gasoline combustion is an additional source of atmos pheric lead in agricultural areas.

3. Due to high zinc emission from individual house holds, and a high proportion of coal combustion in heat ing and electric power production in Poland, it seems essential to establish legislative norms of zinc deposition. Constant Zn monitoring in depositing particulate matter, as well as introducing the standards of its deposition, are necessary.

4. Among all the examined metals Ni was the most stable in the depositing particulate matter and it can be used as a reference element when estimating enrichment coefficients in this Mazowieckie Province region.

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