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TRENDS OF ATMOSPHERIC HEAVY METAL DEPOSITION IN LITHUANIA

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The results of long-term measurements of heavy metal (Pb, Zn, Cr, Ni, Cu, Mn, Cd, Fe, As, Hg) concentrations carried out at the Aukštaitija and Žemaitija integrated monitoring stations (IMS) are presented in this work. The average annual concentrations of heavy metals in the air in 2007–2008 and in precipitation over the period 2006–2010 are analysed. A higher deposited amount of heavy metals on the Earth's surface was determined in the western part of Lithuania (Žemaitija IMS) compared with the eastern part of Lithuania (Aukštaitija IMS). Different deposited amounts of heavy metals are related to higher concentration of heavy metals in the air and higher amounts of precipitation in the western part of Lithuania. A decreasing trend of Pb concentration in precipitation and an increasing trend for Cr, Ni and Cu in precipitation and deposited amounts were observed at both stations. Common correlating groups of element concentrations for both stations were established: As–Cd, Ni–Cr–Cu, and Mn–Cu. These groups are probably typical of the entire territory of Lithuania and are caused by long-range transfer of air masses.

Keywords: heavy metals, concentration, air, precipitation, deposition, trend

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1. Introduction

Heavy metals are emitted into the atmosphere due to industrial, motor transport and volcanic activities, soil erosion, forest fires, evaporation, etc. [1]. Most of metals in the air are in particulate form with the exception of mercury (Hg). Usually, toxic metals such as Pb, Cd, As are found in fine particles (<2.5 μm). Fine particles are respirable and tend to persist in the atmosphere where they can undergo chemical reactions and be transported from their sources over long distances to pristine areas of the environment [2–6]. Most of heavy metals are soluble in water, thus they can migrate in ecosystems by water pathways. Even small amounts and low concentrations of heavy metals can damage ecosystems and are dangerous for human health [7, 8]. Therefore, it is important to know the amount and trends of deposited toxic compounds on the Earth's surface.

Wet and dry deposition is the main process for the removal of particulate metals from the atmosphere and in areas affected by long-range transport of air masses. Direct investigations of chemical compounds in precipitation are always complicated and uncertain in many cases. It is determined that about 40–90% of heavy metals are removed from the atmosphere with wet depositions [9, 10]. Linear relationships between the scavenging coefficients and rain intensity for different aerosol size are observed in [11]. Studies devoted to investigations of atmospheric trace metal deposition are scarce for Central and Eastern European regions [12]. There is a lack of studies where the influence of deposition of long-range transported elements is analysed. During their passage, air masses undergo many transformations which should significantly influence metal concentrations in the air. Experimental results indicated that every location selected for monitoring of pollutants should be evaluated for a possible influence of local sources. Local sources can significantly alter heavy metal concentrations and may be the reason for contrasting results [13].

Anthropogenic emission of heavy metals is not high on the Lithuanian territory, as was shown in our previous paper [14]. The analysis of results

showed that about 10–30% of pollutant amount is washed out by precipitation on the Lithuanian territory. According to the calculations, about 70–90% of pollutants are long-range transported with air masses from Western and Central Europe [15].

Leaded petrol has gradually been ruled out in Europe since 1987 (since 1993 in Lithuania). The application of advanced technologies in Western Europe influenced the air quality in Lithuania. Lead concentration decreased about six times in the atmosphere in Lithuania during 1993–2002 [14]. The rate of emission of some metals (Cd, Pb, Zn) substantially decreased, metal concentrations in the air and in atmospheric depositions dropped with decreased emissions.

During the past decade, a number of studies on atmospheric deposition trends of heavy metals in different areas were published [16–21]. Pb levels were reduced by about 25% during the period 1982–1995, and a slight decreasing trend was found for Co and Hg during the same period. Most of mercury in soil is due to atmospheric deposition, mainly from anthropogenic sources [22]. Deposition of heavy metals is better investigated in background areas than in urban ones. The global pattern shows a decrease of fluxes for most of elements in Paris area during the period 1994–2002 [23].

Recently, a number of studies on spatial, seasonal and annual variations of heavy metal concentrations in ambient air, precipitation and mosses have been published [24–28]. Some results indicated a strong dependence of heavy metal concentration in the air and in precipitation on the amount of precipitation. In general, there are different trends in different regions: atmospheric depositions of most metals were significantly elevated in China compared with other regions, e. g. the Great Lakes region in North America and Northern Europe. The moss method provides a cheap alternative to deposition analysis for identification of areas at risk from high atmospheric deposition fluxes of heavy metals and temporal trends of atmospheric heavy metal deposition across Europe at high resolution. However, it is important to continue studies of heavy metal deposition processes because new anthropogenic sources or increasing emission from other regions may appear.

The aim of the study is to provide variation trends of heavy metal concentrations in the atmospheric deposition and to evaluate possible quantitative changes in Lithuania during the period 2006–2010.

2. Material and methods

2.1. Sampling sites and sampling methodology

Precipitation samples were collected at Aukštaitija and Žemaitija integrated monitoring stations (IMS) in Lithuania (see Fig. 1). The Aukštaitija IMS is located in the east of Lithuania (55°26'N, 26°04'E) and the Žemaitija IMS is located in the west of Lithuania (56°00'N, 21°52'E). The distance between the stations is about 300 km.

The aerosol particle samples were collected at the Aukštaitija IMS from June 2007 through December 2008. The bulk precipitation samples were collected at both stations every week during the period 2006–2010. Three bulk collectors were used at each station. Measurement data from three parallel collectors were averaged to avoid the influence of accidental contamination on the final results.

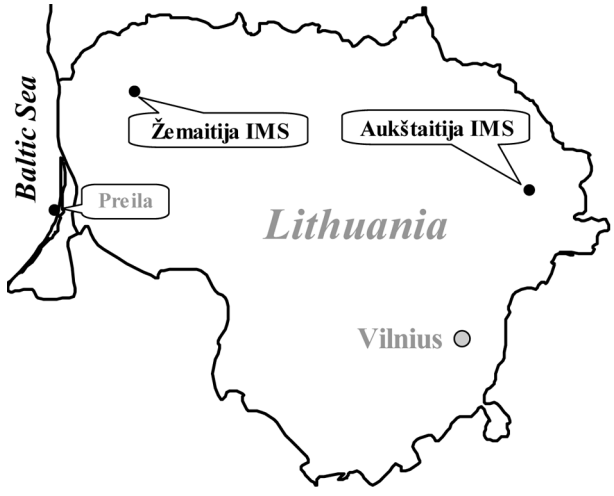

Fig. 1. Scheme of location of sampling stations in Lithuania.

2.2. Preparation procedures for sampling and analysis

Bulk collectors, 1000 ml polyethylene bottles, with funnels 8.15 cm in diameter and 52.15 cm^2 in area were used for sampling of precipitation. Before use, the funnels and bottles were initially soaked in the

5% HNO_3 water solution for three days and later in the 1% HNO_3 water solution for one week. After the above-mentioned procedures they were rinsed with de-ionized water, dried, packed and thus made ready for use. After collection of precipitation, the super clean HNO_3 was added in the collectors to have acid concentration equal to 0.2% per sample and after 24 hours the solution was poured out into clean bottles for storage in the refrigerator at 5 °C temperature. Before storage, the amount of precipitation was registered. The preparation procedure of used collectors was the same as presented above.

The total atmospheric aerosol particles were collected on Whatman filters using a pump and the air flow rate of 1 m^3/h. The filters were changed every three days. After mineralization (digestion of exposed filters with HNO_3 acid) the aerosol samples were ready for analysis. A detailed description of the preparation procedure for sampling is presented in [29].

2.3. Instruments

Concentration of heavy metals in precipitation and aerosol particle samples after preparation were analysed using the Perkin-Elmer *Zeeman 3030* atomic absorption spectrometer. Standard reference materials (NIST 1575 and NIST 1547) were used for checking the calibration procedure. The measurement methodologies were tested every year by EMEP international intercalibration exercises. The results from intercalibration exercises showed that analytical methods used for analysis of environmental samples give reliable and representative results. Detailed information on the procedure of measurements is presented in our previous papers [12–14, 18–19, 25, 29].

3. Results and discussion

3.1. Comparison of average concentration of heavy metals at both stations

The data on monthly average heavy metal concentrations in the air of the Aukštaitija IMS differed 3–10 times during the investigation period. Concentration values in precipitation at each station and between stations varied more significantly (see Table 1). A large disproportion between heavy metal concentrations in the air and

Table 1. Minimal, average and maximal values of monthly heavy metal concentrations in the air, precipitation and deposited amounts at Aukštaitija IMS and Žemaitija IMS (2006–2010).

	Pb	Zn	Cr	Ni	Cu	Mn	Cd	Fe	As	Hg
In air, ng m^{-3} (2007–2008)										
Aukštaitija IMS										
Minimal	0.69	3.33	0.04	0.092	0.37	0.63	0.030	6.80	0.080	
Average	3.38	7.70	0.15	0.277	0.85	3.31	0.105	39.1	0.272	
Maximal	6.22	13.9	0.27	0.440	1.25	6.65	0.305	73.9	0.520	
In precipitation, μg l^{-1}										
Aukštaitija IMS										
Minimal	0.70	3.06	0.027	0.018	0.31	0.218	0.029	19.2	0.047	0.0024
Average	3.54	15.3	0.429	0.703	2.35	4.74	0.129	106	0.267	0.0112
Maximal	14.1	59.7	2.11	2.34	6.69	22.1	0.661	406	1.840	0.0290
Žemaitija IMS										
Minimal	0.266	2.71	0.036	0.014	0.146	1.11	0.013	6.02	0.006	0.0035
Average	6.47	38.4	0.490	2.23	5.64	8.45	0.155	132	0.264	0.0092
Maximal	31.9	551	2.64	16.7	34.9	57.8	1.31	1227	1.65	0.0214
Deposited amounts, μg m^{-2} $month^{-1}$										
Aukštaitija IMS										
Minimal	9.50	59.0	1.10	1.34	14.6	9.7	0.437	222	0.553	0.07
Average	168	699	20.2	34.9	110	235	6.39	4520	12.6	0.63
Maximal	1040	2290	167	262	395	1340	36.9	22500	139	1.99
Žemaitija IMS										
Minimal	27.6	73.3	2.21	2.92	6.32	33.8	0.635	515	0.410	0.035
Average	673	3110	38.4	217	498	639	17.8	8190	28.4	1.13
Maximal	7430	19100	135	1050	2700	2720	136	31900	219	3.58

in precipitation can be explained by irregularity, duration and amount of precipitation during the sampling period. Usually, concentration of heavy metals is higher during short-term than long-term precipitation: the main amount of heavy metals is washed out during the first minutes of rain or snow [30]. The average concentration in precipitation and the deposited amount of heavy metals were higher at the Žemaitija IMS (Table 1). This can be explained by air masses more polluted with heavy metals in the western part of Lithuania and by a higher average yearly amount of precipitation at the Žemaitija IMS (about 1220 mm) than at the Aukštaitija IMS (about 670 mm) (IMS data, 2006–2010).

During the investigation period, the trends of concentrations of heavy metals in the air, in precipitation and in the area unit deposited with precipitation were established. To confirm the reliability of trends, the correlation coefficients of concentrations of heavy metals in the air, in precipitation and in deposited amounts over the sampling time were calculated and are presented in Table 2. Based on the calculation data, the heavy metals with reliable tendencies were determined. The reliability of correlative relation was evaluated based on data presented in [31]. For heavy metals parameters (k, C_0, α, Q_0) of linear regression equations were calculated (Table 3).

The measurement period of heavy metals in the air at the Aukštaitija IMS was relatively short, thus only a decreasing tendency of Cd concentration was identified. A decreasing trend of concentration in precipitation was observed for Pb at both stations and for Fe at the Aukštaitija IMS. Increasing trends were observed for Cr, Ni and Cu at both stations and for Hg only at the Žemaitija IMS. An increasing trend of deposited amounts with precipitation for Cr, Ni and Cu was observed at both stations and for Mn only at the Žemaitija IMS.

A linear regression equation for heavy metal concentration in precipitation is

$$C = k \cdot t + C_0, \tag{1}$$

Table 2. Correlation coefficients between heavy metal concentrations in the air, precipitation and deposited amounts over time.

In air									
Aukštaitija IMS									
Pb	**Zn**	**Cr**	**Ni**	**Cu**	**Mn**	**Cd**	**Fe**	**As**	**Hg**
–0.116	–0.150	–0.141	0.377	–0.002	–0.116	**–0.539**	–0.086	–0.037	
In precipitation									
Aukštaitija IMS									
–0.340	–0.186	**0.559**	**0.428**	**0.333**	0.087	–0.076	**–0.404**	–0.246	–0.081
Žemaitija IMS									
–0.422	–0.201	**0.464**	**0.439**	**0.449**	0.249	–0.060	–0.284	–0.017	**–0.327**
In deposited amounts									
Aukštaitija IMS									
–0.110	–0.045	**0.575**	**0.453**	**0.455**	0.198	0.000	–0.215	–0.195	0.013
Žemaitija IMS									
–0.230	–0.159	**0.594**	**0.419**	**0.414**	**0.434**	–0.046	0.011	–0.117	0.229

Table 3. Coefficients calculated from regression equations.

Element	Average concentration in precipitation, μg l^{-1}				Average deposited amounts, μg $m^{-2}month^{-1}$			
	Aukštaitija IMS		Žemaitija IMS		Aukštaitija IMS		Žemaitija IMS	
	k	C_0	k	C_0	α	Q_0	α	Q_0
Pb	–0.694	5.28	–1.88	11.2				
Cr	0.165	0.015	0.142	0.135	8.52	1.25	13.1	5.67
Ni	0.149	0.330	0.822	0.171	12.3	4.14	73.5	33.4
Cu	0.324	1.54	1.80	1.15	28.5	38.7	150	123
Fe	–23.8	166						
Mn							193	155

where C is the heavy metal concentration in precipitation, k is the annual concentration alteration, C_0 is the concentration from 2006, t is time from the beginning of 2006.

A linear regression equation for deposited amounts of heavy metals with precipitation per month is

$$Q = \alpha \cdot t + Q_0, \quad (2)$$

where Q is the deposited amount of heavy metals to m^2 per month, α is the annual amount alteration, Q_0 is the deposited amount of heavy metals to m^2 per month from the beginning of 2006.

The variation of regression coefficient values of heavy metals is presented in Table 3. The values are presented only for those heavy metals whose correlation coefficients show a reliable relation. Table 3 does not include regression coefficients of Cd concentration in the air over time; they are equal to $k = -0.09$ ng m^{-3} y^{-1} and $C_0 = 0.173$ ng m^{-3}.

3.2. Trends of heavy metals

Pb, Cr and Ni concentration courses and trends in precipitation at the Aukštaitija IMS and Žemaitija IMS are presented in Fig. 2. Deposited amounts of Cr and Ni at both IMSs are presented in Fig. 3. A remarkable increasing of Cr and Ni concentrations from the beginning of 2007 can be seen in Figs. 2 and 3, and it is clearly evident at the Žemaitija IMS. It is hard to relate it with polluted air mass transfer because monthly precipitation amounts were used, while air mass transfer directions were very changeable during a month.

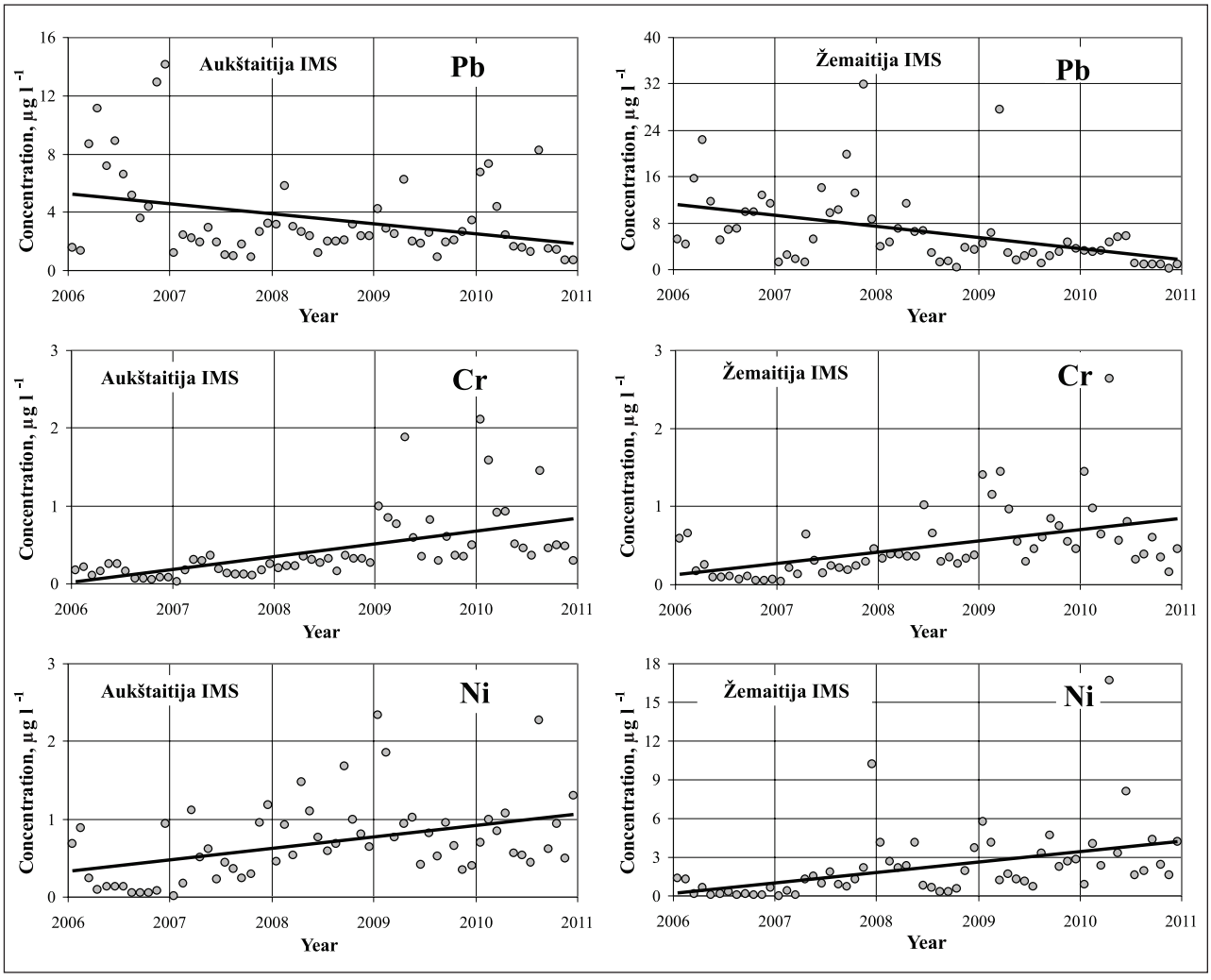

Fig. 2. Trends of Pb, Cr and Ni concentrations in precipitation at Aukštaitija IMS and Žemaitija IMS.

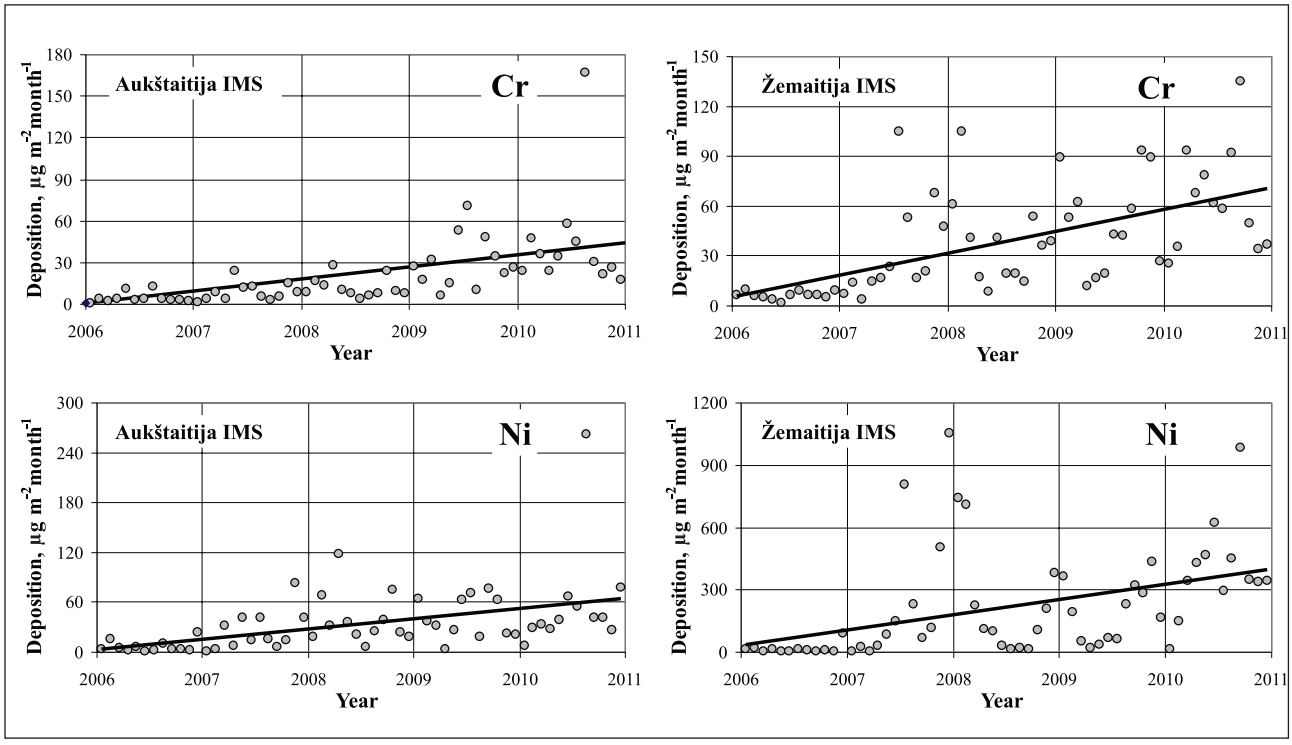

Fig. 3. Trends of deposited amounts of Cr and Ni at Aukštaitija IMS and Žemaitija IMS.

The trends of most deposited heavy metals for the territory of Lithuania were similar at both stations. Our previous investigations of Pb, Cr and Ni concentrations in mosses showed a clear decreasing trend during 1995–2005 [25]; however, the results of our current investigation in precipitation show a contrary trend. We can possibly assume that further research of Cr and Ni in mosses will show an increasing trend of these metals as well.

3.3. Seasonal variations of heavy metal monthly concentration

We consider that the irregularity and different distribution of precipitation over the territory of Lithuania during the investigation period (see Fig. 4) had a large influence on determination of trends of heavy metals.

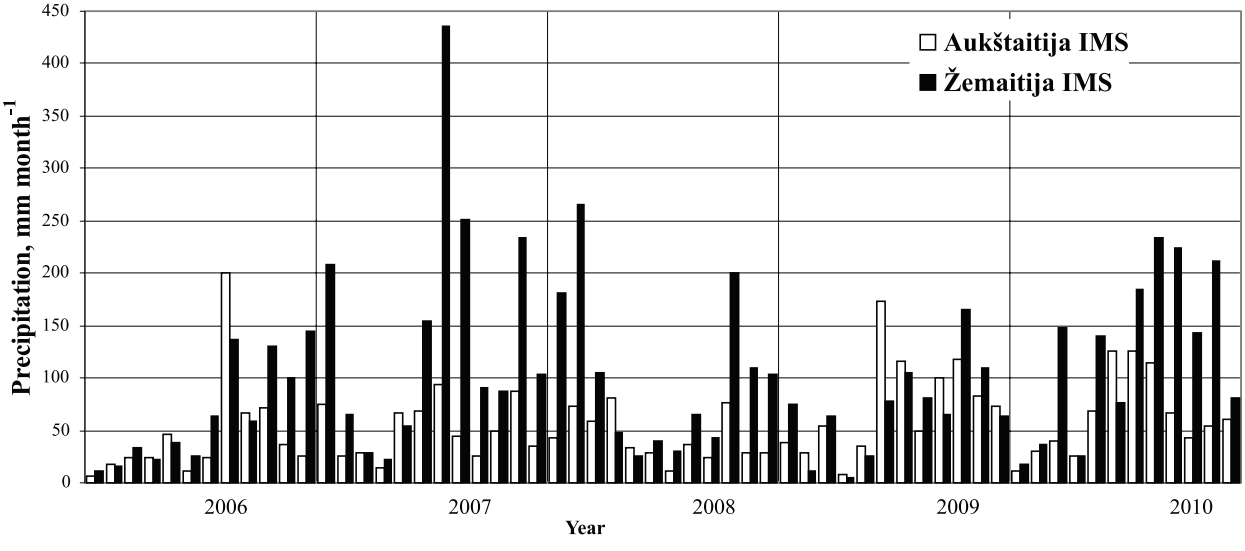

Fig. 4. Average monthly precipitation amounts at Aukštaitija IMS and Žemaitija IMS.

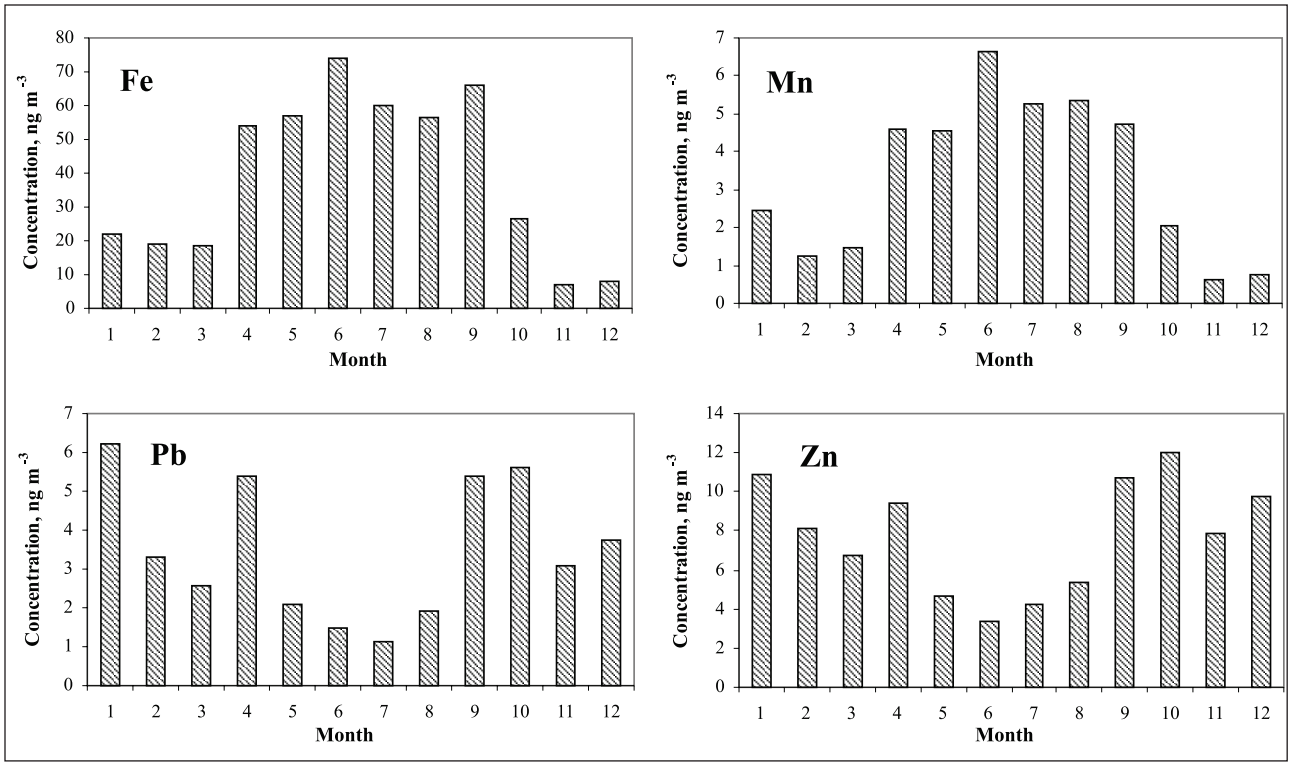

Fig. 5. Average monthly concentrations of Fe, Mn, Pb and Zn in the air at the Aukštaitija IMS (2007–2008).

A comparison of the seasonal variation of heavy metals in the air and in precipitation showed that concentration variations in the air were more clearly expressed than in precipitation (see Fig. 5).

A comparison shows that Fe and Mn (natural origin) and Pb and Zn (anthropogenic origin) have a contrary seasonal variation (Fig. 5). Fe and Mn are emitted to the atmosphere and their concentrations in the air are higher during the warm season. For elements of anthropogenic origin, higher concentrations in the air are observed during the cold period because of larger fuel consumption during the heating season, decreased turbulent air mixing, and different air mass transfer frequency. The analysis of air mass backward trajectories shows that most frequently air masses are coming to Lithuania from west and northwest [15]. The lowest frequency distribution is for the air masses coming to Lithuania from east and south. Such a clear seasonal variation in the air as described above is not observed for heavy metal concentrations in precipitation or deposited amounts (see Fig. 6). The main reason is precipitation irregularity and different distribution on the Lithuanian territory.

Correlation coefficients of heavy metal concentrations in precipitation at the Aukštaitija IMS and Žemaitija IMS are presented in Table 4. Common correlating element groups for both stations are identified and marked in bold in the table: As–Cd, Ni–Cr–Cu, and Mn–Cu. Probably, the above-mentioned groups are typical of the entire territory of Lithuania and are caused by long-range transfer of air masses. Monthly concentrations of heavy metals Pb, Zn, Cr, Ni, Cu, Cd and As in the air at the Aukštaitija IMS were measured in 19 samples. Concentrations of Fe and Mn were measured throughout the year 2008 (12 samples). Two heavy metal groups with strong correlation can be selected from these measurement data: Zn–Pb–As (correlation coefficient 0.878–0.968) and Fe–Mn (correlation coefficient 0.980).

Correlation coefficients between concentrations of Mn and Fe in the air and in precipitation are 0.577 and 0.650, respectively. Data analysis shows that these correlating groups do not have recurrence for heavy metal concentrations in the air and the deposited amount. This can be explained by a different amount of data obtained at the stations: only 12–19 measurements in the air

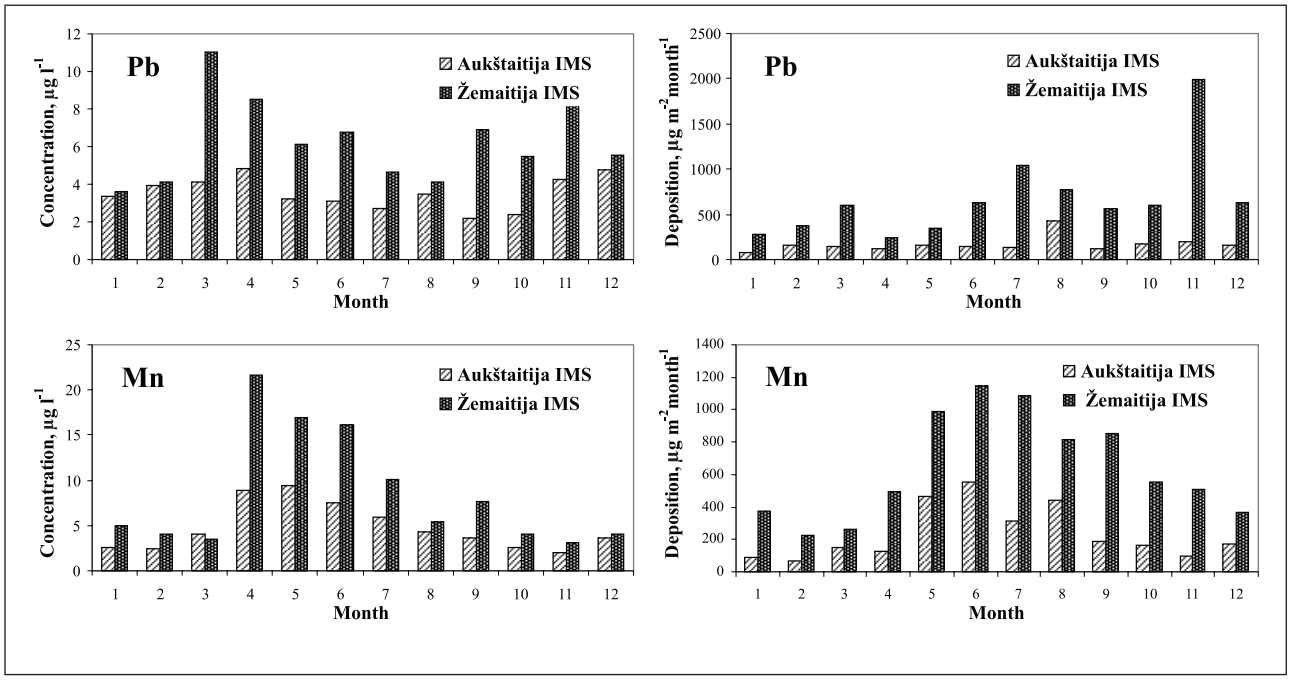

Fig. 6. Average monthly concentrations in precipitation and deposited amounts of Pb and Mn at Aukštaitija IMS and Žemaitija IMS (2006–2010).

Table 4. Correlation coefficients of heavy metal concentrations in precipitation at Aukštaitija IMS and Žemaitija IMS. Numbers in bold indicate reliable correlation.

Aukštaitija IMS										
	Pb	**Zn**	**Cr**	**Ni**	**Cu**	**Mn**	**Cd**	**Fe**	**As**	**Hg**
Pb	1.000	–0.008	0.148	–0.071	–0.204	0.038	0.059	0.221	0.111	0.110
Zn		1.000	–0.104	**0.424**	**0.462**	0.095	0.251	**0.548**	**0.410**	0.278
Cr			1.000	**0.487**	**0.505**	0.314	0.229	–0.163	–0.040	–0.033
Ni				1.000	**0.557**	0.013	0.305	–0.037	0.165	0.041
Cu					1.000	**0.418**	0.249	0.163	0.135	0.162
Mn						1.000	0.240	0.325	0.020	–0.063
Cd							1.000	–0.037	**0.702**	–0.262
Fe								1.000	0.114	**0.391**
As									1.000	–0.070
Hg										1.000
Žemaitija IMS										
	Pb	Zn	Cr	**Ni**	**Cu**	**Mn**	**Cd**	**Fe**	**As**	**Hg**
Pb	1.000	–0.014	–0.089	–0.124	–0.161	–0.136	0.298	0.001	0.052	–0.392
Zn		1.000	0.077	0.129	0.173	0.110	0.206	0.095	0.144	–0.214
Cr			1.000	**0.668**	**0.772**	**0.511**	0.041	0.191	0.328	0.195
Ni				1.000	**0.866**	**0.566**	**0.492**	0.178	**0.741**	0.054
Cu					1.000	**0.624**	0.202	0.126	**0.583**	–0.003
Mn						1.000	0.083	0.229	**0.435**	0.169
Cd							1.000	–0.001	**0.649**	–0.242
Fe								1.000	**0.372**	0.260
As									1.000	–0.012
Hg										1.000

Table 5. Average concentration of heavy metals in the air, ng m^{-3} (2007–2008).

	Pb	Zn	Cr	Ni	Cu	Mn	Cd	As	Fe
Preila EMEP station	5.47	14.5	0.318	0.803	1.84	3.35	0.127	0.476	50.1
Aukštaitija IMS	3.36	7.63	0.150	0.282	0.851	3.32	0.102	0.270	39.1

at the Aukštaitija IMS were performed, and about 40–60 measurements of heavy metal concentrations in precipitation were performed at both stations. Another reason for the absence of the above-mentioned recurrence is different distribution of elements on different-size aerosol particles, which can impact different washout effectiveness from the atmosphere [11]. The third reason is the already-mentioned irregularity of precipitation, e. g. different intensity and distribution at both stations during the investigation time.

Because the measurements of heavy metals in the air were performed only at the Aukštaitija IMS, for comparison of results we used the heavy metal data in the air from the Preila EMEP background station which is located only 85 km away from the Žemaitija IMS in the western part of Lithuania. The data obtained at this station during the same period (from the beginning of June 2007 till the end of 2008) can be used to compare heavy metal concentrations in the air of eastern and western parts of Lithuania (see Table 5).

It can be seen in Table 5 that heavy metal concentrations in the air are remarkably higher in the western part of Lithuania, as was stated above.

4. Conclusions

A higher deposited amount of heavy metals on the earth was observed in the western part of Lithuania (at the Žemaitija IMS) compared with the eastern part of Lithuania (at the Aukštaitija IMS). This difference was probably due to a higher concentration of heavy metals in the air and a higher amount of precipitation in the western part of Lithuania. A decreasing trend of Pb concentration in precipitation and an increasing trend for Cr, Ni and Cu in precipitation and deposited amounts were observed at both stations. Heavy metal concentrations in the air had seasonal variation at the Aukštaitija IMS. Concentrations of natural origin elements (Fe and Mn) were higher during the warm period, while anthropogenic origin elements (Pb, Zn, Cr, Ni, Cu, Cd, As, Hg) had higher concentrations during the cold period. The common correlating groups of elements for both stations were established: As–Cd, Ni–Cr–Cu and Mn–Cu. These groups are probably typical of the entire territory of Lithuania and are caused by long-range transfer of air masses. For confirmation of the above conclusion, further investigations are needed.

Acknowledgements

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SUNKIŲJŲ METALŲ NUSĖDIMO IŠ ATMOSFEROS TENDENCIJOS LIETUVOJE

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Santrauka

Pateikti ilgalaikių sunkiųjų metalų (Pb, Zn, Cr, Ni, Cu, Mn, Cd, Fe, As, Hg) koncentracijų matavimų Aukštaitijos ir Žemaitijos integruoto monitoringo stotyse (IMS) rezultatai. Vidutinės metinės sunkiųjų metalų koncentracijos ore ir krituliuose eigos analizė pateikta 2006–2010 metams. Vakarinėje Lietuvos dalyje nustatyta didesnė žemės paviršiaus apkrova sunkiaisiais metalais negu rytinėje dalyje. Tikriausiai šis paviršiaus apkrovos skirtumas susidarė dėl didesnės sunkiųjų metalų koncentracijos ore ir didesnio kritulių kiekio vakarinėje Lietuvos dalyje. Stebėta Pb koncentracijos krituliuose mažėjimo tendencija abiejose IMS bei Cr, Ni ir Cu koncentracijos krituliuose ir iškritose į žemės paviršių didėjimo tendencija abiejose stotyse. Nustatytos bendros koreliuojančių metalų As–Cd, Ni–Cr–Cu ir Mn–Cu koncentracijų grupės abiems stotims. Tikimiausia, kad šios grupės yra būdingos visai Lietuvos teritorijai ir yra nulemtos tolimosios oro masių pernašos.