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Influence of iron ore works in Nižná Slaná on the atmospheric deposition of heavy metals

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The contribution deals with an evaluation of atmospheric deposition monitoring in 2001–2009 which was realised in the vicinity of siderite mining and processing works. Besides of gaseous emissions the works also produced the solid compounds of iron oxides and other heavy metals. The iron ore plant worked up to August 2008. The atmospheric deposition (wet and dry) was determined by the modified bulk deposition methodology. The samples were collected from seventeen monitoring sites, which are located maximally up to 8 km from the main pollution source. Together with the deposition fluxes of heavy metals (Fe, Mn, Zn, Pb, Cu,Cr, Cd, As), the mineralogical composition, dispersion and size characteristics of solid particles were studied in selected samples. The volume content of respirable solid particles with the diameter under 5 μm was from 6.7 to 13.2 %. Nanoparticles with the average hydrodynamic diameter in the interval of 242–558 nm were found. High values of the deposition (median) of iron - 4111 mg.m^{-2}.year^{-1}, manganese - 236.6 mg.m^{-2}.year^{-1} and especially toxic arsenic - 8.05 mg.m^{-2}.year^{-1} were measured in the area of Nižná Slaná in the years 2001–2008 and compared with other areas. A correlation between emissions of solid pollutants in particular years and the deposition for these metals was observed. In 2009, after shutdown of the works, a decrease of values at the most contaminated sites of deposition by arsenic, manganese and iron about 90 % was recorded. Such a significant change was not recorded for other studied metals.

Keywords: *atmospheric deposition, heavy metals, iron ore works, emissions*

Introduction

Atmospheric concentrations of hazardous substances are affected by natural and anthropogenic processes. The content of heavy metals in the atmospheric deposition significantly contributes to the pollution of environment. For this reason a lot of studies deals with the research of atmospheric deposition, mostly using methods of wet and dry deposition (bulk deposition), wet deposition, but also methods using fog water e.g. Azimi et al., 2003; Fišák et al., 2002; Golomb et al., 1997; Lawlor et al., 2003; Nicholson et al., 2003; Prášková et al., 2006; Sandroni et al., 2003; Spiegel et al., 2003; Wong et al., 2003.

The emissions from the technologies of ores and industrial minerals processing by their specific composition influence the constitution of atmospheric deposition, especially in the areas of processing plants. After sedimentation, the components of atmospheric deposition interact with soil and other constituents of environment and in such a way directly influence their quality. The main emission source in the area of Nižná Slaná was iron-ore mining and processing works. The plant mined the siderite ore. The ore was processed into the blast furnace pellets as a final product of the plant. The production was stopped in August 2008. Besides gas emissions, the plant produced also solid emissions, mainly iron oxides with a content of heavy metals. The contribution deals with the evaluation of results obtained from monitoring of atmospheric deposition by the modified bulk deposition methodology. The research was carried out in the area of the Siderite, Ltd. from 2001 to 2009, predominantly from viewpoint of selected heavy metals deposition (Fe, Mn, Zn, Pb, Cu, Cr, Cd, As) and the influence of the plant on it. The particle size and morphological characteristics of solid particles were studied too.

Characteristics of the plant, meteorological conditions and solid emissions

The plant is situated in the Slaná river valley in the vicinity of Rožňava town. The valley has an orientation of north-south and northwest-southeast, respectively. The wind circs are influencing by an orography of given territory. Distribution of wind directions and the occurrence of calm in the near-by Rožňava town are shown in Table 1 (Kyntera et al., 1984). Directions of wind oriented across the valley are not often. There is evident the prevalence of north and south winds. Exploited deposit is located in the Revúca upland Mts., the Dobšiná foothill belt Mts. of the Slovak Ore Mts. formed by the rocks of early Palaeozoic (Grecula et al, 1995). Siderite is utility mineral. The average content of iron and manganese in ore is 33.5 % and 2.8 %, respectively. Manganese is bonded isomorphically in the siderite lattice. There are also unfavourable elements (As, S, Pb, Zn) that occur as sulphides, sulphates, sulphosalts and oxides. The most significant unacceptable impurity is arsenic that is present in the form of arsenopyrite. The average content of As in the run-off-mine ore is approximately of 0.01–0.1 % (Mihók, 1997). Ore processing consisted of crushing, magnetizing roasting, wet milling, magnetic separation and pelletizing. Primarily, thermal technologies, i.e. pelletizing and magnetizing roasting were responsible for the amount of dust outlet. Flue gases were exhausted to the environmental air through 120-meter

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high chimney after several stages of dedusting. Table 2 presents the average concentrations of the selected elements in the dust outlet from pelletizing plant and rotary furnaces (Fedorová, 2003). The emissions of solid pollutants from 1998 to 2009 are showed in Table 3. The emissions of solid pollutants were lowest in 2002 (32.9 t), because the production in the plant was stopped for five months. The highest amount of emissions, i.e. 155.8 t was recorded in 2006. Finally, the emission level was of 89.4 t in 2008.

Tab. 1. Percentage of the wind directions and calm in the Rožňava town.

N	N-E	E	S-E	S	S-W	W	N-W	Calm
38	8	6	2	25	2	3	6	10

Tab. 2. The content of the selected elements in the solid dust outlets from thermal technologies.

Technology	Fe	Mn	Zn	Pb	Cu	Cr	Cd	As
	[%]		[ppm]					
Pelletizing	30.4	3.48	94	32.6	99	39	25	636
Rotary furnaces	27.8	2.12	200	127	170	63	24	176

Tab. 3. The emissions of solid pollutants from the plant [t.year^{-1}].

1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
156.4	116.3	116.9	86.7	32.9	63.3	63.8	121.5	155.8	148.4	89.4	0

Material and methods

The samples of atmospheric deposition were taken in the 30 days (±3 days) intervals from the seventeen sampling stations. In 2009, the samples were evaluated from the fourteen sites. The sampling sites no. 3, 5 and 9 were destroyed. The localization of sampling stations is illustrated in Fig. 1. The opened cylindrical plastic sedimentation containers (inside diameter – 12.5 cm), put in two support stands in the height of 2.5 to 3 m, were used for the sampling. The containers were filled with 250 ml of deionized water with 10 % content of isopropanol which is a non-polar liquid. After sampling, the content of containers was quantitatively located to evaporating dishes and evaporated. The organic mass was removed by annealing of dry matter at 450 °C. The chosen temperature prevented carbonate degradation and in such way enables to avoid the misinterpretation of total deposition gravimetry results. The samples from 2009 were not annealed due to small weighed portion of the samples. The selected unannealed samples of solid phase after treatment by ultrasound were also subjected to granulometric and morphological analysis. The dispersion and the particle size analysis were done using laser granulometer HELOS/LA (Sympatec) by the suspension cell wet method (CLCELL) and particles with diameter under 1 μm were measured by NANOPHOX particle sizer (Sympatec) using the photon cross correlation spectroscopy (PCCS) wet method. The morphological properties of particles were studied by scanning electron microscope (SEM) on the apparatus TESLA BS 340. The samples for chemical analysis were prepared by cumulation of twelve monthly ones into the one and by mineralization using microwave decomposition (MWS-3, Berghof). The heavy metals were measured through the use of F-AAS and GF-AAS method (Varian SpectrAA 240FS/240Z and SpectrAA–30). On the basis of chemical analyses and mass of the obtained analyte, the annual depositions fluxes by observed heavy metals were calculated. The values of the average deposition and the values of the basic statistical parameters (minimum, maximum, average, median) for the period 2001-2008 and 2009 are presented in the table 4. The medians from all sampling sites were used for the calculation of the correlation coefficient between emissions of solid pollutants and deposition fluxes of the monitored metals in the individual years.

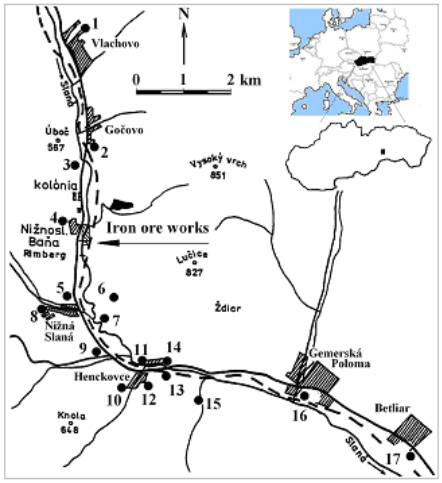

Fig. 1. The localization of the sampling sites in the area of Nižná Slaná.

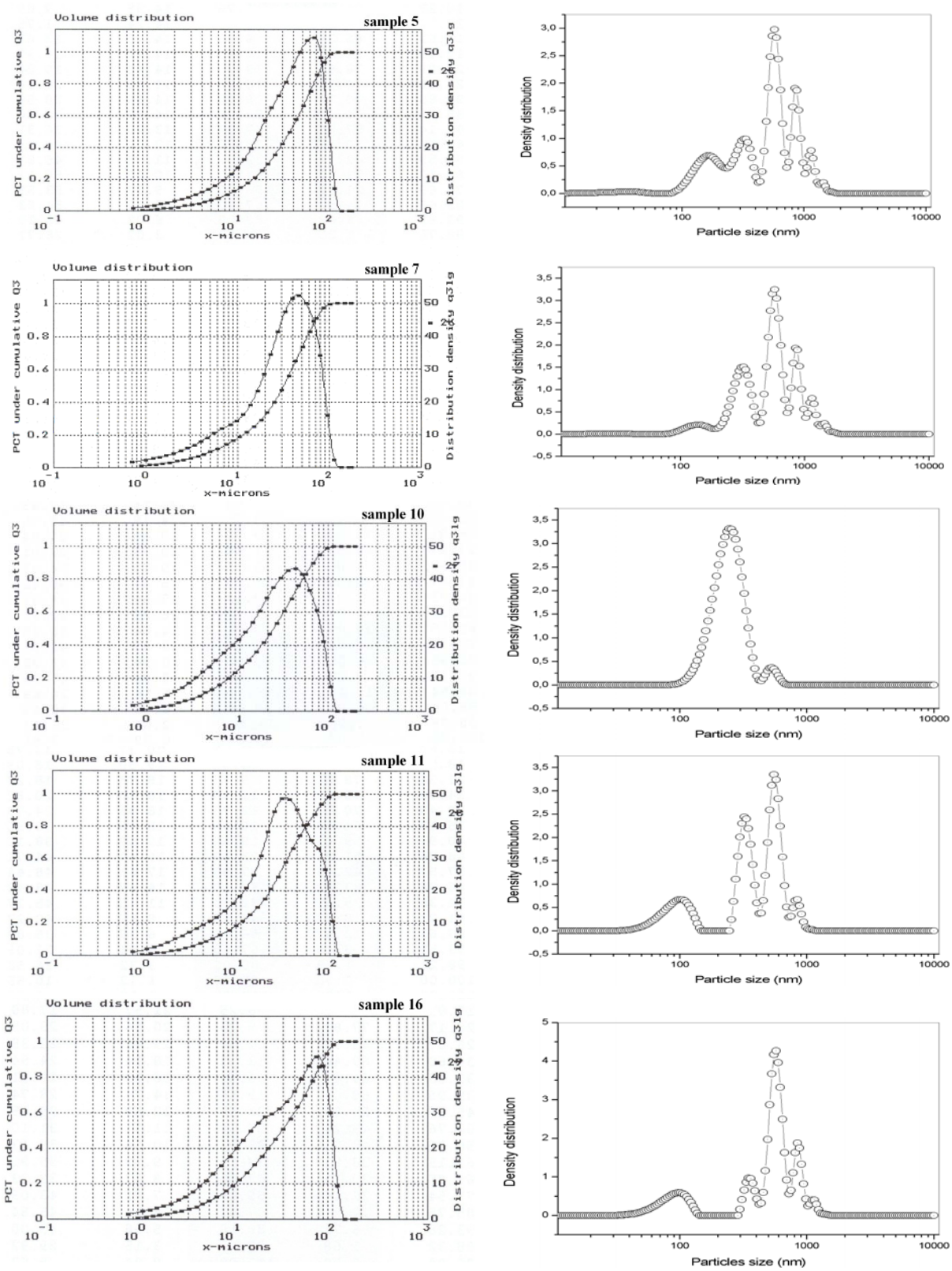

Fig. 2. Basic granulometric curves of samples from sampling sites No. 5, 7, 10, 11 a 16, output from the apparatus HELOS (left) and NANOPHOX (right).

Results and discussion

Granulometric analysis

The size of particles markedly influence their ability of transport. The granulometric analyses of particles from atmospheric deposition were measured in sampling sites No. 5, 7, 10, 11 and 16 from samples collected in 2008. The granulometric analysis was not possible for all sites due to insufficient amount of sample. The dispersion and the particle size analysis of these samples are shown in Fig. 2. The values of average hydrodynamic diameter of particles were in the interval 23–36 μm. The volume contents of particles with diameter under 10 μm were in the range 13.9–25.8 %. The contents of respirable solid particles with diameter under 5 μm attained 6.7–13.2 %. The smallest mean hydrodynamic particle diameter, and also the highest proportion of particles under 10 μm and 5 μm was recorded at site No. 10. This site is at a distance from the main source of emissions (120 m high chimney) in the direction of the main wind flow of approx. 3.2 km. The values of the mean aerodynamic diameter of particles are continuously increasing from this point. Generally, heavy metals are predominantly bonded on particles with diameter under 10 μm (Eštoková et al., 2008). The occurrence of particles with hydrodynamic diameter under 1 μm was confirmed by measuring on the device Nanophox (measuring range of 10–10,000 nm). The nanoparticles with the average hydrodynamic diameter in the interval of 242–558 nm were found. The smallest mean hydrodynamic diameter of these nanoparticles was also observed in the sample from sampling site No. 10. The grain size curves are significantly polydisperse, it advert to the origin these particles from different technological processes in the works.

Morphological analysis

The morphological properties of these particles were studied. The SEM photographs of selected samples are shown in Fig. 3. The particles of different morphological habits and their aggregates and agglomerates were observed. Various sharp fracture particles, prismatic particles, fused-on particles, particles with planes of cleavage, expanded spherical particles and various other shapes of particles were observed in the samples. The occurrence of carbonates in the samples was indicated by calcite cleavage, content of alumosilicates are confirmed by the occurrence of spherical porous structures. In the past, the samples of solid phase of atmospheric deposition were also subjected to XRD analysis (Baluchová et al., 2004). Thus, minerals such as quartz, chlorite, siderite, ankerite were detected. These minerals come from raw ore handling but also as a result of aeolation from surrounding environment. On the other side hand there are minerals, namely hematite, maghemite, magnetite and wüstite coming from the thermal technologies of the works. The photos confirmed the occurrence of very fine particles in the samples. The amount of fine particles was adhered to the surface of large particles. The morphologically and granulometric properties of particles in analyzed samples refer to marked representation of particles which are coming from the technology of the works.

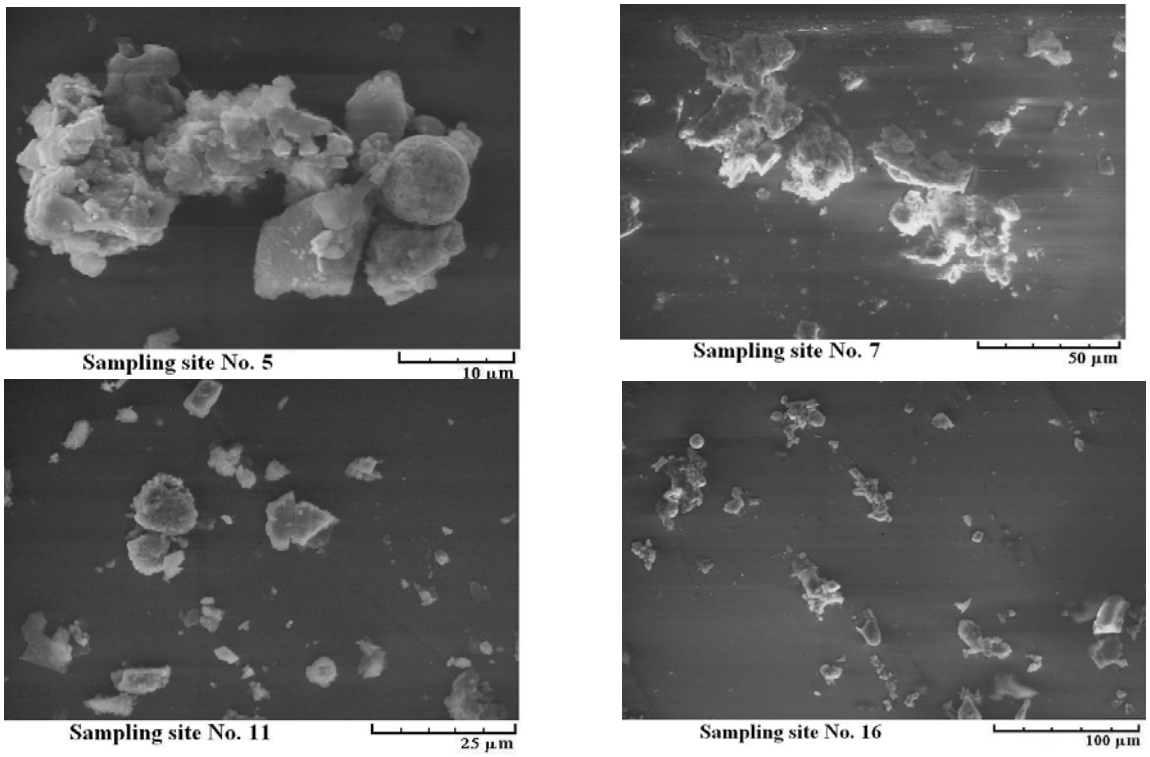

Fig. 3. SEM photos - morphological characteristics of particles from selected samples at different magnification.

Analysis of atmospheric deposition

Table 4 presents average values of deposition of heavy metals in the area of Nižná Slaná in 2001–2008, in 2009 and basic statistic parameters for the whole monitored period and all sampling sites. The qualitative composition of atmospheric deposition significantly contributed to the ecological load of the individual sampling points that was caused by works activities.

Tab. 4. The average deposition fluxes of selected heavy metals in the area of Nižná Slaná in 2001-2008 and 2009 and basic statistic parameters for the whole monitored period and all sampling sites [mg.m^{-2}.year^{-1}].

Sampling site	Fe		Mn		Zn		Pb	
No.	2001-2008	2009	2001-2008	2009	2001-2008	2009	2001-2008	2009
1	2324	1700	71.3	21.0	22.5	18.1	1.72	0.37
2	3290	581	198.6	13.3	12.1	10.2	0.84	0.43
3	4930	-	276.9	-	56.9	-	1.19	-
4	5176	675	309.5	23.5	14.6	11.7	0.79	0.36
5	10658	-	645.5	-	18.6	-	2.11	-
6	6311	756	407.5	24.3	17.8	11.4	1.01	0.29
7	9269	512	626.7	18.7	43.5	52.4	1.70	0.49
8	1746	577	58.6	19.6	11.9	14.0	0.46	0.66
9	4899	-	302.5	-	65.1	-	0.72	-
10	3774	471	256.4	7.5	9.5	10.6	0.57	0.45
11	4717	579	291.2	12.1	15.3	12.4	0.80	0.32
12	2331	462	137.4	10.5	9.5	37.8	0.55	0.53
13	4542	459	279.4	12.9	16.7	14.9	0.65	0.40
14	6131	1238	327.0	18.4	22.9	350.4	1.55	2.41
15	3959	1042	222.6	22.5	13.7	11.6	0.59	0.43
16	5312	905	291.4	26.2	23.5	32.5	2.80	1.61
17	1228	950	65.1	38.9	13.0	10.6	0.60	3.83
Average	4741	779	280.4	19.2	22.8	42.8	1.10	0.90
Min.	192	459	23.1	7.5	3.2	10.2	0.01	0.29
Max.	18231	1700	1106.6	38.9	198.4	350.4	10.63	3.83
Median	4111	628	236.6	19.1	14.9	13.2	0.39	0.44
Sampling site	**Cu**		**Cr**		**Cd**		**As**	
No.	**2001-2008**	**2009**	**2001-2008**	**2009**	**2001-2008**	**2009**	**2001-2008**	**2009**
1	2.69	3.36	2.87	2.06	0.058	0.018	2.88	2.16
2	2.74	1.93	4.07	0.97	0.031	0.019	8.53	0.77
3	3.71	-	2.76	-	0.058	-	9.41	-
4	3.80	2.62	3.53	0.76	0.051	0.023	16.34	0.82
5	6.04	-	2.96	-	0.037	-	31.29	-
6	3.53	1.71	4.10	0.98	0.037	0.024	16.80	1.03
7	5.31	2.16	3.00	1.60	0.070	0.039	23.48	1.00
8	2.58	2.51	1.33	1.73	0.051	0.028	1.49	0.45
9	3.49	-	2.69	-	0.055	-	8.84	-
10	2.72	2.79	1.54	1.09	0.038	0.018	7.30	0.36
11	3.05	1.96	1.90	1.13	0.039	0.019	10.04	0.47
12	1.94	1.62	1.42	1.06	0.030	0.026	3.23	0.58
13	3.28	2.02	2.18	0.86	0.033	0.034	12.57	0.43
14	4.17	2.91	2.45	1.07	0.055	0.027	15.89	1.56
15	3.18	4.04	3.87	1.73	0.043	0.021	11.24	1.05
16	3.98	5.69	2.90	1.97	0.058	0.066	16.53	0.61
17	1.73	3.79	1.23	0.62	0.046	0.030	2.72	3.12
Average	3.41	1.26	2.63	1.26	0.046	0.028	11.68	1.03
Min.	0.23	1.62	0.26	0.62	0.003	0.018	0.16	0.36
Max.	9.20	5.69	17.79	2.06	0.182	0.066	48.50	3.12
Median	3.25	2.56	2.28	1.08	0.038	0.025	8.05	0.80

Among various sampling sites high differences in the deposition were determined mainly for Fe, Mn and As from 2001 to 2008 during the operation of the works. The highest values were measured in the sampling sites localized south of the plant, in its vicinity, i.e. No. 5 and No. 7. The lowest values were detected in the sampling sites No. 8, in the distance of 1.7 km from the main chimney and No. 17 (its distance was approximately 8 km from the main chimney). The sampling site No. 8 is situated on the west side of the valley and it is slightly influenced by chimney plume. This fact is confirmed by measured concentrations of monitored heavy metals. There were not so high differences in the deposition of others elements. The most ecological load was situated in the south of the plant, in the central part of the valley. The statistical dependence between emissions of solid pollutants and deposition of observed metals (annual median) in the individual years (except 2009) by correlation analysis was evaluated (Hančuľák et al., 2008, 2009). Relatively high positive values of correlation coefficient were calculated for manganese, iron and arsenic, namely 0.750, 0.704 and 0.652, respectively. Correlation coefficients for other elements were relatively low or negative. The development of selected metal

deposition fluxes (median) and the emissions of solid pollutants for the whole monitoring period are shown in Table 5 and Fig. 4, respectively.

Tab. 5. Annual medians of deposition (all sampling sites) and correlation coefficients between emissions of solid pollutants and deposition fluxes of heavy metals [mg.m^{-2}.year^{-1}].

Year	Fe	Mn	Zn	Pb	Cu	Cr	Cd	As
2001	3453	175.2	16.3	1.40	3.14	1.69	0.032	1.52
2002	3506	187.2	20.7	0.34	3.98	2.67	0.085	3.42
2003	2381	136.6	12.4	0.14	2.55	1.79	0.051	9.94
2004	3069	194.7	15.2	0.16	3.30	1.74	0.063	5.67
2005	4718	302.9	11.8	0.23	2.44	2.29	0.034	12.99
2006	4746	278.8	12.3	0.26	2.50	2.44	0.038	11.50
2007	7690	436.8	14.0	1.45	3.48	2.61	0.014	16.90
2008	5801	319.3	11.9	1.90	3.32	2.56	0.010	15.76
Correlation coef.	0.704	0.750	-0.616	0.206	-0.473	0.310	-0.703	0.652

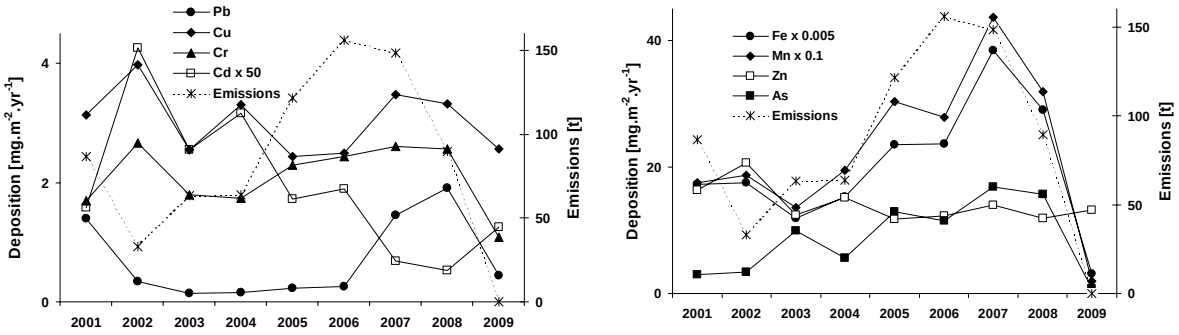

Fig. 4. Development of selected metal deposition fluxes (median) and the emissions of solid pollutants.

In 2009 after shutdown of the works, the significant decrease values of deposition of manganese, arsenic and iron was observed compared with the previous years. The values of deposition of iron were lower by 22.6–94.7 % (versus average 2001–2008) at all sampling sites. The deposition of manganese decreased by 40.2–97.1 %. The values of deposition of arsenic were reduced by 14.9–96.6 %. Only in one case (the most distant sampling site No. 17) the values increased. The twofold decrease was observed in the case of chromium. The origin of chromium was probably from the abrasion of rotary furnaces lining containing chromite. A very slight decrease was observed in atmospheric deposition of copper and cadmium. Comparable values were measured in the case of zinc and lead. They were slightly higher than in the previous period. The comparison of observed metal and their deposition fluxes for the whole monitoring period and the all sample sites (median) is shown in Fig. 5.

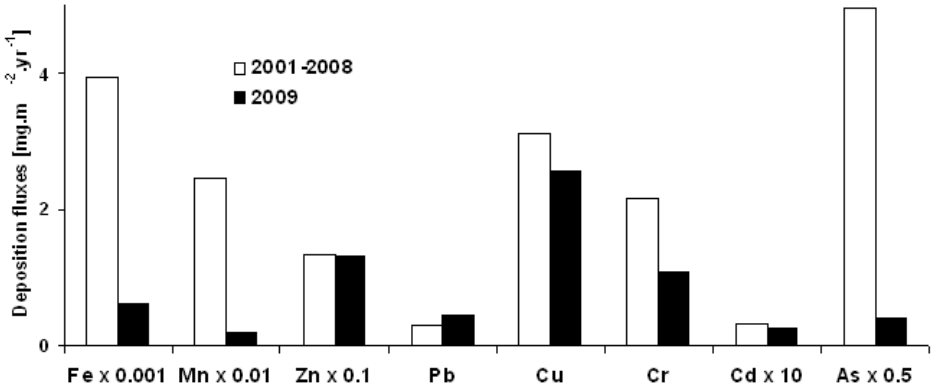

Fig. 5. Comparison of deposition fluxes heavy metals before (2001 –2008) and after (2009) the shutdown of the plant.

In the Slovak Republic there are not determined allowable limits for heavy metals loading from atmospheric deposition. That is the reason why relative comparison of heavy metal depositions for different localities is used for assessment of immission load. The values of atmospheric deposition of heavy metals in this study were compared with results from another localities and they are shown in Tab. 5. The localities of industrial areas in Slovakia (Hančuľák et al., 2005; Ursíniová et al., 1992), selected agricultural areas in Czech republic (Prášková et al., 2006), measured for subsystems of basic and contaminated areas, agricultural areas in Austria (Spiegel et al., 2003) and England (Nicholson et al., 2003), urban and suburban areas in China (Wong et al., 2003) are compared there.

In the Nižná Slaná locality, deposition of iron achieves high values because of solid pollutants emissions consist mainly of iron minerals, namely oxides. The depositions monitored in the individual stations were in the range from 192 (site No. 17 in 2005) to 18,636 mg.m^{-2}.year^{-1} (site No. 7 in 2007), the average deposition was of 4,741 mg.m^{-2}.year^{-1}. In Košice town with metallurgy industry, the values varied from 232 to 7,568 mg.m^{-2}.year^{-1}. In Czech Republic in 2005 (measured for subsystems of basic and contaminated areas), ten times lower iron deposition was determined in comparison with area of Nižná Slaná (69–1,002 mg.m^{-2}.year^{-1}). In 2009 the average deposition of iron decreased to normal value 779 mg.m^{-2}.year^{-1} in the area Nižná Slaná.

Tab. 6. Comparison - atmospheric deposition of heavy metals of different location [mg.m^{-2}.year^{-1}].

Location		Fe	Mn	Zn	Pb	Cu	Cr	Cd	As
Nižná Slaná (2001 – 2008)[a]	**Average**	4741	280.4	22.8	1.10	3.41	2.63	0.046	11.68
	Median	4111	236.6	14.9	0.39	3.25	2.28	0.038	8.05
	Minimum	192	23.1	3.2	0.01	0.23	0.26	0.003	0.16
	Maximum	18231	1106.6	198.4	10.63	9.20	17.79	0.182	48.50
Nižná Slaná (2009)[a]	**Average**	779	19.2	42.8	0.90	2.79	1.26	0.028	1.03
	Median	628	19.1	13.2	0.44	2.56	1.08	0.034	0.80
	Minimum	459	7.5	10.2	0.29	1.62	0.62	0.018	0.36
	Maximum	1700	38.9	350.4	3.83	5.69	2.06	0.066	3.12
Jelšava (1996 –2003)[b]	**Average**	-	227.4	62.4	8.32	17.44	10.52	0.678	4.70
	Minimum	-	112.3	40.2	3.29	15.21	8.15	0.511	0.99
	Maximum	-	406.4	77.7	17.52	20.81	12.53	1.119	7.73
Krompachy (1998 – 1999)[b]	**Average**	-	8.1	39.4	9.20	38.57	1.87	1.265	4.09
	Minimum	444	4.6	11.1	2.49	4.52	0.95	0.237	0.23
	Maximum	3902	13.6	100.5	21.89	128.26	4.04	3.862	14.59
Košice (1998 – 1999)[b]	**Average**	-	34.4	59.6	4.54	6.71	9.13	0.742	0.30
	Minimum	232	18.2	21.7	1.48	4.64	2.78	0.102	0.10
	Maximum	7568	48.2	85.8	9.18	10.55	14.62	1.433	0.71
Slovakia (1986 –1989)[c]	**Maximum**	-	668	1880	380	304	108	6.700	35.00
Czech Republic Basic areas (2005)[d]	**Average**	231	13.1	50.6	1.75	7.52	0.50	0.065	0.22
	Minimum	69	5.0	9.0	1.03	1.20	0.21	0.025	0.09
	Maximum	566	68.3	120.1	4.47	113.76	0.93	0.185	0.53
Czech Republic Contaminated areas (2005)[d]	**Average**	291	13.6	54.3	8.77	2.88	0.67	0.148	0.47
	Minimum	83	5.4	18.0	1.13	1.15	0.21	0.030	0.01
	Maximum	1002	34.2	206.0	119.91	5.13	2.81	1.230	2.11
England and Wales (1995 –1998)[e]	**Average**	-	-	22.1	5.4	5.7	0.75	0.190	0.31
	Minimum	-	-	12.6	1.9	3.2	0.29	0.070	0.09
	Maximum	-	-	35.6	13.9	24.7	2.00	0.610	1.00
China (2001 – 2002)[f]	**Average**	555	9	104	12.7	18.6	6.4	0.07	-
	Minimum	311	5	36	2.9	10.7	3.7	0.01	-
	Maximum	923	14	164	25.4	40.9	16.2	0.15	-
Austria (1999-2001)[g]	**Minimum**	-	-	21.4	1.90	6.24	0.72	0.146	-
	Maximum	-	-	48.9	5.44	14.70	1.95	0.325	-

[a] – the present study, [b] – (Hančuľák et al., 2005), [c] – (Ursíniová et al., 1992), [d] – (Prášková et al., 2006), [e] – (Nicholson et al., 2008), [f] – (Wong et al., 2008), [g] – (Spiegel et al., 2008)

The highest contents of manganese in atmospheric deposition were detected in the area of Nižná Slaná and Jelšava with maximum of 1106.6 and 406.4 mg.m^{-2}.year^{-1}, respectively. Average values exceeded 200 mg.m^{-2}.year^{-1}. After shutdown of the iron ore works in Nižná Slaná, these values were in the range 7.5–38.9 mg.m^{-2}.year^{-1} . In past in Slovakia (1986–1989), the most manganese loaded territory was the locality Dolný Kubín that is located nearby iron-alloy works Istebné, where the maximum deposition manganese value from dust fallout was 668 mg.m^{-2}.year^{-1}. In other parts of Slovakia, average deposition of manganese was 4.6 and 34.4 mg.m^{-2}.y^{-1} in the Krompachy and Košice, respectively. In the case of Nižná Slaná and Jelšava, the main manganese sources were iron-ore mining works, magnesite works and raw materials (siderite, magnesite) treated in these works. In the Czech Republic in the monitored territories the average deposition of Mn was 13.6 mg.m^{-2}.year^{-1} and the maximum deposition was 68.3 mg.m^{-2}.year^{-1}, in urban an suburban areas in China the values were measured in the range 5–14 mg.m^{-2}.year^{-1}.

The deposition values of zinc in the Nižná Slaná area were in the interval 3.2–198.4 mg.m^{-2}.year^{-1} with the average value of 22.8 mg.m^{-2}.year^{-1} in 2001–2008. In 2009 the median of zinc deposition was 13.2 mg.m^{-2}.year^{-1}, the maximum value 350.4 mg.m^{-2}.year^{-1}, which was measured in 2009 is probably random. In general, these values are not very high for industrial areas. In the Czech Republic, the average atmospheric depositions of zinc were 50.6 and 54.3 mg.m^{-2}.y^{-1} and the maximum was 206 mg.m^{-2}.year^{-1}. In the agricultural area Austria and England, the measured values of zinc deposition were in the range from 21.4 to 48.9 mg.m^{-2}.year^{-1} and from 22.1 to 35.6 mg.m^{-2}.year^{-1}, respectively. In China the average value 104 mg.m^{-2}.year^{-1} was measured.

The deposition of lead was relatively low (median 0.39 mg.m^{-2}.year^{-1} in 2001–2008 in the locality of Nižná Slaná). In 2009 the values were comparable with previous years, median – 0.44 mg.m^{-2}.year^{-1}. The high deposition of lead (21.89 mg.m^{-2}.y^{-1}) in Slovakia was measured in Krompachy, while the main source of solid pollutions was copper smeltery. In past, in Slovakia, there was determined the maximum deposition of Pb in dust fallout (380 mg.m^{-2}.year^{-1}) in the locality of Prievidza, that was caused by steam brown coal combustion. The deposition of lead was 5.4 to 13.9 mg.m^{-2}.year^{-1} in England and Wales. In Austria and China, the measured values were 1.90–5.44 mg.m^{-2}.year^{-1} and 2.9–25.4 mg.m^{-2}.year^{-1}, respectively.

The deposition of copper reached low values in Nižná Slaná, median was 3.25 mg.m^{-2}.year^{-1} before shutdown in the works, 2.56 mg.m^{-2}.year^{-1} in 2009. High copper deposition (128.26 mg.m^{-2}.year^{-1}) was measured in Krompachy nearby copper smeltery, when the works operated only partially in 1998–1999. In past 1986–1989, maximum value 304 mg.m^{-2}.year^{-1} was registered in Bratislava. The values in Austria and England were in range from 6.24 up to 14.70 mg.m^{-2}.year^{-1}, respectively 22.1 to 35.6 mg.m^{-2}.year^{-1}. In China the deposition of copper was 10.7–40.9 mg.m^{-2}.year^{-1}.

The median of chromium depositions in Nižná Slaná was 2.28 mg.m^{-2}.year^{-1} in 2001–2008, in 2009 the value decreased to 1.08 mg.m^{-2}.year^{-1}. The average depositions of chromium from dust fallout in Krompachy and Jelšava were 1.87 and 10.52 mg.m^{-2}.year^{-1}, respectively. The maximum measured value was detected in Košice (14.62 mg.m^{-2}.year^{-1}). The main chromium emission sources of these areas in Slovakia are metallurgy and chromite additions to furnace lining and their abrasions. In Slovakia, the highest deposition of chromium 108 mg.m^{-2}.year^{-1} was registered nearby of Sereď nickel smeltery in the past. In the Czech Republic, atmospheric deposition monitoring revealed values in the range from 0.21 to 2.81 mg.m^{-2}.year^{-1} and in Austria in the interval from 0.72 to 1.95 mg.m^{-2}.year^{-1}. In England and Wales, the chromium values were in range from 0.75 to 2 mg.m^{-2}.year^{-1}. In China, the deposition of chromium attained 3.7 – 16.2 mg.m^{-2}.year^{-1} .

The deposition values of cadmium in the Nižná Slaná were in the range from 0.003 to 0.182 mg.m^{-2}.year^{-1}. These are relatively low values. In Košice and Jelšava, the measured average values were 0.678 and 0.742 mg.m^{-2}.year^{-1}, respectively. The high values in the range 0.237–3.862 mg.m^{-2}.year^{-1} were measured in the Krompachy area. In Slovakia, the highest deposition of cadmium – 6.7 mg.m^{-2}.year^{-1} was measured nearby cement works in Rohožník during 1986–1989. In the Czech Republic, the atmospheric deposition monitoring detected the values in the range from 0.025 to 1.230 mg.m^{-2}.year^{-1} and in Austria in the range 0.146–0.325 mg.m^{-2}.year^{-1}. The deposition of Cd from 0.07 to 0.61 mg.m^{-2}.year^{-1} was referred from England and Wales. Low values 0.01–0.15 mg.m^{-2}.year^{-1} were registered in China.

Very high values of arsenic deposition were measured in the area of Nižná Slaná during iron ore works operating. The source of arsenic was arsenopyrite, which occurred in run-off-mine siderite ore. The values in the monitored areas were in the range 0.16–48.50 mg.m^{-2}.year^{-1}, the median was 8.05 mg.m^{-2}.year^{-1}. The maximum arsenic value was detected from sampling station No. 5 that is close to the works. This value is two fold times higher that the maximum value from Krompachy, where 14.59 mg.m^{-2}.year^{-1} was measured. In past, in the Slovak Republic, maximum of arsenic deposition was 35 mg.m^{-2}.year^{-1} nearby thermal power station in Nováky (effect of steam brown coal combustion with high concentration of arsenic). In 2009 the deposition of arsenic significantly decreased in the area Nižná Slaná. The values in the range of 0.36–3.12 mg.m^{-2}.year^{-1} and median 0.80 mg.m^{-2}.year^{-1} were observed. The average values for atmospheric deposition in the Czech Republic were 0.50–0.67 mg.m^{-2}.year^{-1} and maximum arsenic value was 2.11 mg.m^{-2}.year^{-1} in 2005. In England and Wales, the As values were in the range from 0.31 to 1 mg.m^{-2}.year^{-1}.

Conclusion

The monitoring and analysis of atmospheric deposition in the vicinity of Nižná Slaná has shown the influence of iron-ore mining and processing works on the extent of ecological load of this area. The significant quantity of solid fines originated in the works was observed in samples of atmospheric deposition. In comparison with atmospheric deposition from others localities, this area was the most influenced by iron, manganese and especially toxic arsenic. This fact reflected the composition of siderite ore and applied technological processes in the works. After shutdown of the plant, the significant decrease values of deposition of manganese, arsenic and iron was observed compared with the previous years. Although relatively small territory was monitored, the significant differences are detected. There are many different factors, for example:

meteorological, orographic, emissive, binding and particle sedimentation mechanisms with linkage to impurities, etc.

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