Influence of Iron and Steel Industry on Selected Elements of Atmospheric Deposition in the Urban and Suburban Area of Košice (Slovakia)

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Abstract

The contribution deals with the atmospheric deposition (AD) of selected elements in the typical urban area with many sources of pollution. The main sources of pollution are represented by nearby iron and steel works and the thermal power station. Qualitative and quantitative characteristics of the total deposition of solid particles, the deposition fluxes of elements Fe, Al, Mn, Zn, Pb, Cu, Cr, Cd, As, their seasonal variations and the development of deposition these elements were studied. The eleven sampling sites have been placed on the roof above the height of the surrounding buildings at a distance of between 1 and 15 kilometers from the iron and steel works. The results from the years of 2009–2014 are introduced. The maximum values of AD for all studied metals and particles were recorded at sites localized southerly, near the ironworks (No. 9, 10). The average ratio between AD at site No. 9 and sites for the observed elements were in the range 2.3 to 19.8. Slightly higher deposition fluxes of all studied metals (RW/S = 1.18–1.35) except Al, As and partially in the case Zn, were found in winter. The smallest seasonal differences were detected at sites near the ironworks and the thermal power station. The highest values of correlation coefficients (r = 0.90 to 0.97) were calculated between AD of elements where their dominant source are technologies of ironworks, namely Mn, Fe and Cr. At sites the south of the ironworks the presence of all observed metals in the insoluble phase is predominated and their representation is relatively higher. The extremely high values AD of iron, manganese and the over-average deposition of chromium were measured at sites near the ironworks as compared to the deposition of the other areas. The moderate increase of the deposition of iron, manganese, chromium and partially in the case of lead and zinc was observed in the recent times.

Keywords: atmospheric deposition fluxes, solid particles, emission, metallurgy

Introduction

Transition of substances from the atmosphere to the surface is happening by atmospheric deposition processes. These processes are often the main input of various pollutants to other environmental components. Specific anthropogenic emissions from the large sources of pollution influence on the composition of atmospheric deposition (AD). The study of qualitative composition AD and deposition fluxes of its components can be a suitable instrument for identifying sources of pollutants, their spatial distribution, variability, mass fluxes and environment quality. For this reason, many research studies deal with AD from point of view of various parameters and aspects (Azimi et al., 2005; Davis and Birch, 2011; Golomb et al., 1997; Hančuľák et al., 2011, 2014; Nicholson et al., 2008; Wong et al., 2008). The Košice area, in addition to typical urban pollution sources such as road traffic, municipal sphere, small industrial sources and construction is long-term environmental loaded by the iron and steel works – the largest source of pollution in Slovakia. The paper presents some results of the AD monitoring predominantly from viewpoint of deposition fluxes of selected elements (Fe, Al, Mn, Zn, Pb, Cu, Cr, Cd and As) and solid particles in relation to emissions from large industrial sources in the area of Košice.

Characteristics of the area

The monitored area is located in the Košice Basin, in the river valley Hornád with north-south orientation in the eastern part of Slovakia. The Košice has about 234,000 inhabitants. The wind conditions are determined by the orography of the valley. There is evident prevalence of north (53.5%) and south (31.6%) winds, occurrence of calm is 9.5%. The average annually amount of precipitation is 625 mm, mean annually temperature is 8.5°C. Except emissions arising from small industrial and municipal sources, road traffic and civil engineering, two large industrial and energetics sources of pollutants are located in its vicinity and directly in the city. It is mainly complex iron and steel works – U.S. Steel Košice, which is located about 10 km southward – south-westward from the centre of city (annual emissions of solid pollutants, SO_2 and NO_x – 3,000; 8 000 and 6,000 tons respectively in 2009–2013). The thermal power station which is situated directly in the southern part of the city emitted about 100; 1,100 and 1,500 tons of solid emission, SO_2 and NO_x per year. The solid emissions produced by sources of iron and steel works are qualitatively different. Operation of ore sintering accounted for 55%, coke plants 24%, blast furnaces 15%, energetics 3%, steel works 2% and other sources produce of 1% in 2012 (NEIS, 2015). In the complex iron and steel works also operates lime works (60–300 tons of solid emissions per year) and several other smaller sources of pollution tied to the metallurgical industry.

Materials and methods

Total atmospheric deposition i.e. both wet and dry ones, were collected monthly from eleven sites in the urban and suburban area in vicinity iron and steel works, from June 2009 to October 2014. The sampling sites were at a distance of 1–15 km from the main source of pollution. The localization of sampling sites is illustrated in Fig. 1. The four open polyethylene cylinders (inside diameter – 12.5 cm and 16 cm height) fitted on a stand were used for sampling. In the urban area, the sites no. 1–6 were placed on the top roof of block flats and public building at 24–36 m height from the ground level, above the height of surrounding buildings, 4–12 m in the case suburban sites no. 7–11. The containers were filled with 200 ml of pure deionized water. In laboratory the contents of cylinders were filtered on a vacuum filtration through 0.40 μm membrane filters to separate the "water soluble" and "insoluble" fractions. The soluble fraction af-

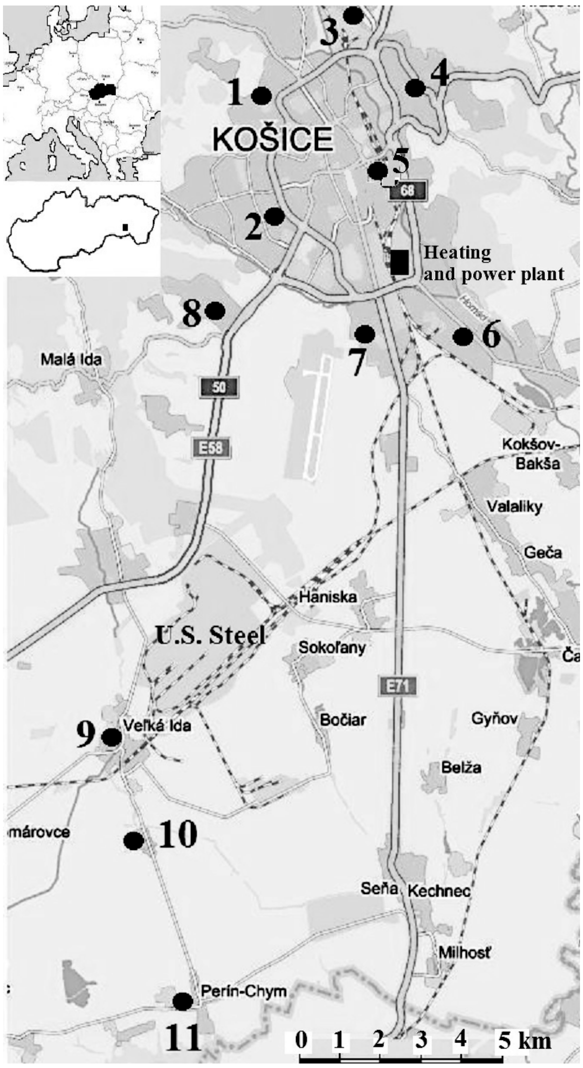

Fig. 1. Location of the sampling sites

Rys. 1. Lokalizacja miejsc pobierania próbek ter filtration was prepared for chemical analysis. The insoluble fraction for analysis was prepared by cumulation of six monthly samples into the one -semi-annual sample – summer and winter period (May – September, October – April) and by mineralization using a microwave digestion MWS-3 Berghof. The trace metals were analyzed by the atomic absorption spectroscopy using the device VARIAN AA240 FS with Programmable Sample Dispenser PSD 120, GTA 120 and VGA-77 and by ICP- MS Agilent 7700.

Results and discussion

In table 1 are processed daily deposition fluxes of solid particulates – SP ("water insoluble" phase AD), monitored elements and the average ratio of their deposition in winter and summer – ratioW/S. Absolute values of deposition monitored components from monitoring stations north of ironworks are relatively balanced, without increased values at station No.5. The site is situated in the centre of city with heavy traffic and high construction activities during monitored period, about 2 km northward of the thermal power station, which uses coal except gas as fuel mainly in heating season.

The maximum values of all studied metals and SP were recorded at sites localized southerly, near the ironworks. The average ratio between atmospheric deposition at site No. 9 and sites No. 1- 8 (ADSite 9/ADSites 1-8) for the observed elements were in the range 2.3 to 19.8 (Fe = 8.5, Al = 4.2, Mn = 19.8, Zn = 2.9, Pb = 5.1, Cu = 5.8 , Cr = 7.4, Cd and As = 2.3).

Deposition of solid particles is significantly higher in summer period (ratioW/S – 0.6). There are better conditions for eolian erosion and resuspension particles from soil horizon, road traffic, agricultural and construction activities as well as the increased presence of organic detritus in the air

Tab. 1. The average daily fluxes of solid particles (SP) and analyzed elements from 6 summer and 5 winter monitored periods (Summer 2009 – Summer 2014), [$\mu g.m^{-2}.day^{-1}$]

Tab. 1. Średnie dzienne opady cząstek stałych (SP) I analiza 6 okresów letnich I 5 okresów zimowych (lato 2009 – lato 2014) [$\mu g.m^{-2}.day^{-1}$]

Site	SP	Fe	Al	Mn	Zn	Pb	Cu	Cr	Cd	As
1	38401	2797	942	61	96	9.3	11.2	7.1	0.35	0.76
2	40776	2818	1050	59	74	8.4	8.7	6.5	0.27	1.01
3	44820	2721	958	57	91	8.9	9.0	5.6	0.31	0.77
4	42376	3453	1052	64	80	7.6	9.7	5.1	0.28	1.21
5	90402	5155	1810	98	120	12.1	18.3	9.1	0.36	1.30
6	31465	2698	861	52	67	6.2	8.7	4.9	0.22	0.49
7	43962	4089	1131	78	100	8.6	9.3	7.3	0.28	1.09
8	33046	3038	1045	73	136	8.7	9.0	6.0	0.31	0.61
9*	172768	27232	4396	1295	259	42.9	57.5	45.9	0.68	1.87
10*	126180	18551	2897	695	195	21.6	15.7	21.7	0.35	1.30
11*	52791	4288	1278	75	113	9.5	10.3	4.9	0.20	1.67
**Ratio $_{W/S}$	0.58	1.34	0.72	1.34	0.89	1.18	1.32	1.27	1.35	0.62

* Winter 2011- 2012,

** Ratios of winter and summer fluxes – average from all sites

Tab. 2. The Pearson´s cross-correlation coefficients between fluxes of trace elements (n = 106)

Tab. 2. Korelacja wzajemna Pearsona przepływu pierwiastków (n=106)

	Al	Mn	Zn	Pb	Cu	Cr	Cd	As
Fe	0.83	**0.97**	0.49	0.76	0.55	**0.90**	0.48	0.29
Al	-	0.82	0.43	0.67	0.42	0.79	0.35	0.34
Mn	0.82	-	0.50	0.77	0.57	**0.93**	0.50	0.25
Zn	0.43	0.50	-	0.59	0.32	0.47	0.50	0.12
Pb	0.67	0.77	0.59	-	0.37	0.80	0.67	0.22
Cu	0.42	0.57	0.32	0.37	-	0.61	0.26	0.19
Cr	0.79	**0.93**	0.47	0.80	0.61	-	0.53	0.27
Cd	0.35	0.50	0.50	0.67	0.26	0.53	-	0.10
As	0.34	0.25	0.12	0.22	0.19	0.27	0.10	-

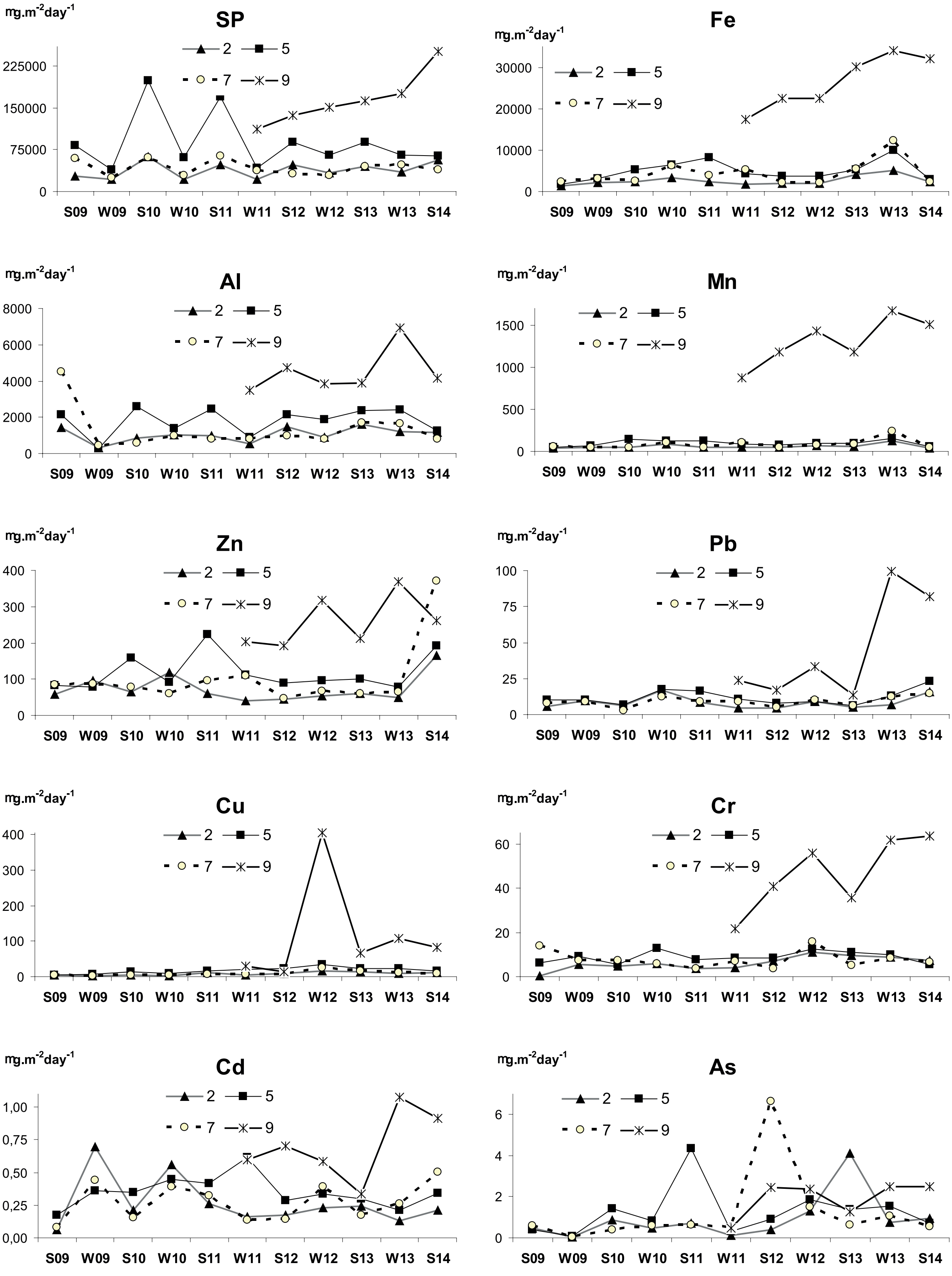

Fig. 2. The development of AD of insoluble fraction (SP) and monitored elements from the sites No. 2,5,7 and 9, (S09 – summer period 2009, W09 – winter period 2009–2010,…S14 – summer period 2014)

Rys. 2. Wpływ zawartości fazy stałej AD i badanych pierwiastków z punktów nr 2,5,7 I 9, (S09 – lato 2009, W09 – zima 2009-2010...S14 – lato 2014) in summer period. In winter, the deposition fluxes of solid particles are partially deprived of these effects. In winter seasons it is assumed increased amount of components of AD, whose origin is in energy burning of fossil fuels in local and regional scale. In the area of Košice, slightly higher deposition fluxes of all studied metals (R W/S = 1.18 –1.35) except Al (R W/S = 0.72) and As (R W/S = 0.62) and partially in the case Zn (R W/S = 0.89) were found in winter. The smallest seasonal differences were detected at sites near the ironworks (No. 9 and 10) and the station No. 5.

The statistical dependence between depositions of observed elements were evaluated by Pearson´s correlation analysis. The Pearson´s cross-correlation coefficients are summarized in Table 2. The highest values of correlation coefficients (r = 0.90 to 0.97) were calculated between elements where their dominant source are technologies of ironworks, namely Mn, Fe and Cr. The relatively high values of the correlation coefficients were calculated for these elements with Al (r = 0.79 to 0.83), Pb (r = 0.61 to 0.77) and Cu (r = 0.55 to 0.61), relatively lower with Zn (r = 0.47 to 0.50) and Cd (r = 0.48 to 0.53), the lowest values were detected in the case of As (r = 0.27 to 0.29).

In table 3 is shown the average percentage representation of the deposition of trace elements bound to the "water-insoluble" (solid particulates) phase for each sampling point. To the insoluble phase, the monitored elements in order of Al, Fe, Cr, Pb and As are bounded. For stations north of ironworks, Cd and Zn are preferentially bounded to the soluble phase. South of the ironworks representation of all observed metals in the solid insoluble phase is predominated and their representation is relatively high. Except monitored elements properties it is probably related with average size and thus with the surface of the particles. With increasing distance from the source of particulate emissions, proportion of smaller particles on their overall particle size distribution is rising.

The deposition fluxes of the elements from the area of Košice were compared with results from different areas. The AD of observed elements from rural areas in Czech Republic, England, Wales, Austria and USA, urban and suburban areas in Serbia, France and China (Prášková et al., 2008; Nicholson et al., 2008; Spiegel et al., 2008; Golomb et al., 1997; Mijić et al., 2011; Azimi et al., 2005; Wong et al., 2008) were compared with the results from the study. In this comparison above average deposition of Fe, Cr and partially in the case of Zn and Mn was detected. The most significant differences were found for the deposition of iron. The average Fe deposition at stations in the city was 2–3, respectively 5–7 times higher compared with rural respectively urban areas. At the station No. 9, deposition of Fe and Mn was 15 or 38 times higher, deposition of Cr 2.5 or 6 times higher. The station is located approximately 1 km from the largest industrial source of solid pollutants in Slovakia. The values of other observed elements were comparable with their average values measured in the urban environment.

The development of overall insoluble fraction AD (SP) and monitored elements for the whole monitored period consisting of 6 summer and 5 winter periods from selected sampling sites is

Tab. 3. The average element abundances in insoluble phase (SP) [%]

Tab. 3. Średnia liczebność pierwiastków w fazie nierozpuszczalnej (SP) [%]

Site	Fe	Al	Mn	Zn	Pb	Cu	Cr	Cd	As
1	98.0	99.1	70.0	32.5	77.9	42.1	76.5	31.3	61.8
2	98.4	99.4	73.1	36.6	72.1	60.5	92.1	33.7	46.9
3	97.6	99.4	75.8	33.5	72.2	57.7	76.0	29.1	59.5
4	98.3	99.3	70.8	35.3	78.4	54.9	94.2	52.0	85.5
5	99.2	99.6	89.6	65.4	79.2	60.3	89.6	51.8	84.2
6	97.7	99.2	69.6	36.9	72.6	47.1	84.9	31.1	76.8
7	98.5	98.9	71.8	36.7	77.0	50.7	77.1	40.2	84.8
8	98.4	98.7	67.8	23.2	74.7	44.5	75.6	29.4	70.4
9	99.9	95.6	97.6	92.4	90.3	78.9	97.5	81.6	86.7
10	99.9	97.5	94.7	79.4	93.2	66.0	97.3	81.8	86.2
11	99.6	98.9	91.8	70.2	60.4	43.9	83.9	68.2	90.0
Average	**98.7**	**98.7**	**79.3**	**49.3**	**77.1**	**55.1**	**85.9**	**48.2**	**75.7**

graphically presented in the figure 2. The absolute values for site No. 9 are order of magnitude greater compared to the values from sites locations in the city for most of the monitored elements. Also, at all sampling sites can be observed high level of seasonal variability AD. The specific increase of absolute values of deposition was observed in the case of elements closely related to ironworks emission sources, namely with iron, manganese, chrome and insoluble fractions AD (SP) mainly on the sampling sites located south of the ironworks - the most significant was in winter period of 2012–2013. Partially, the increase was also recorded in the case of lead and cadmium. The emissions of solid polluting substances from the ironworks tended to increase from 2368 tons in year 2009 to 3302 tons in year 2013 (NEIS, 2015). As it is generally known in addition to emission conditions the variability of meteorological and climatic factors has significant influence on absolute values of components of AD.

Conclusion

The atmospheric bulk deposition, its qualitative and quantitative characteristics were studied by deposition fluxes of selected elements and solid particles from 11 sampling sites in the urban and suburban area of Košice in vicinity of the largest industrial source of solid pollutants in Slovakia. The results pointed to the impact of the ironworks and the thermal power station on AD of observed components. The above-average values of deposition fluxes of iron were determined at sampling stations in the city of Košice, The highest values of all observed parameters were measured in the sampling site (No. 5) in the centre of city. The extremely high values of deposition of iron, manganese and the over-average deposition of chromium were measured at sites (No. 9, 10) near the ironworks as compared to the deposition of the other areas. The moderate increase of the deposition of iron, manganese, chromium and partially in the case of lead and zinc was observed in the recent times.

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Wpływ przemysłu żelaza i stali na emisję wybranych pierwiastków do atmosfery na terenach miejskich i podmiejskich w mieście Košice

Praca traktuje o emisji do atmosfery (skrót AD) wybranych pierwiastków w typowej przestrzeni miejskiej, gdzie istnieje wiele źródeł zanieczyszczenia. Główne źródła zanieczyszczeń na badanym terenie to pobliskie huty żelaza i stali oraz elektrownia cieplna. Zbadano charakterystykę ilościową i jakościową całkowitej depozycji cząsteczek stałych, strumień depozycji pierwiastków Fe, Al, Mn, Zn, Pb, Cu, Cr, Cd, As i ich wahania sezonowe, oraz rozwój depozycji wymienionych pierwiastków. Tereny testowe zostały wybrane w 11 miejscach na dachach okolicznych budynków w odległościach od 1 do 15 kilometrów od hut żelaza i stali. Przedstawiono wyniki z lat 2009-2014. Najwyższe wartości AD dla wszystkich badanych metali i cząsteczek zostały odnotowane na terenach południowych, w pobliżu hut (No. 9, 10). Średni współczynnik AD między terenem nr 9, a terenami obserwowanych pierwiastków mieścił się w zakresie od 2,3 do 19,8. W zimie odnotowano nieco wyższy strumień depozycji wszystkich badanych metali (RW/S = 1,18 – 1,35) poza Al, As i częściowo Zn. Najniższe różnice sezonowe zostały odnotowane na terenach położonych niedaleko hut i elektrowni cieplnej. Najwyższe wartości współczynników korelacji (r = 0,90 do 0,97) zostały wyliczone między AD pierwiastków, których głównym źródłem występowania są technologie związane z hutnictwem, dokładniej Mn, Fe oraz Cr. Na terenach na południe od hut, obecność wszystkich obserwowanych metali w fazie nierozpuszczalnej była przeważająca, a ich poszczególna reprezentacja relatywnie wyższa. W porównaniu do innych terenów, depozycja w pobliżu hut osiągnęła ekstremalnie wysokie wartości dla żelaza, manganu oraz wartości powyżej średniej dla chromu. Umiarkowany wzrost depozycji żelaza, manganu, chromu i częściowo ołowiu oraz cynku zaobserwowano niedawno.

Słowa kluczowe: odcieki opadów atmosferycznych, faza stała, emisja, metalurgia