



Influence of the Copper Smeltery in Krompachy (Slovakia) on Atmospheric Deposition

Jozef HANČUEĀK¹⁾, Tomáš KURBEL²⁾, Daniel KUPKA³⁾, Tomislav ŠPALDON⁴⁾,
Ol'ga ŠESTINOVÁ⁵⁾, Lenka FINDORÁKOVÁ⁶⁾, Erika FEDOROVÁ⁷⁾

¹⁾ Ing., Ph.D.; Institute of Geotechnics of the Slovak Academy of Sciences, Watsonova 45, 040 01 Košice; email: hanculak@saske.sk

²⁾ Mgr.; Institute of Geotechnics of the Slovak Academy of Sciences, Watsonova 45, 040 01 Košice; email: kurbel@saske.sk

³⁾ MVD., Ph.D.; Institute of Geotechnics of the Slovak Academy of Sciences, Watsonova 45, 040 01 Košice; email: dankup@saske.sk

⁴⁾ Ing.; Institute of Geotechnics of the Slovak Academy of Sciences, Watsonova 45, 040 01 Košice; email: spaldon@saske.sk

⁵⁾ Ing., Ph.D.; Institute of Geotechnics of the Slovak Academy of Sciences, Watsonova 45, 040 01 Košice; email: sestinova@saske.sk

⁶⁾ Ph.D.; Institute of Geotechnics of the Slovak Academy of Sciences, Watsonova 45, 040 01 Košice; email: findorakova@saske.sk

⁷⁾ Dr. Ph.D.; Institute of Geotechnics of the Slovak Academy of Sciences, Watsonova 45, 040 01 Košice; email: fedorova@saske.sk

Summary

The samples of atmospheric deposition, i.e. the both wet and dry ones, were collected in the area Krompachy in the vicinity of the copper smeltery during 2009 – 2013. The sampling was realized by means of seven sites located from 1.2 to 10 km of main source of pollution. Major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , SO_4^{2-} , NO_3^- , Cl^- , F^-) and trace elements (Fe, Al, Mn, Zn, Pb, Cu, Cr, Cd, As) were assayed.

The atmospheric deposition fluxes of trace elements were determined separately for "water soluble" and "insoluble" phase. An influence of the sampling sites distance from the copper smeltery on the absolutely values of major ions were not recorded. On the other hand the deposition of trace elements is clearly effected by the copper smeltery operation. The ions fluxes which have origin in gaseous precursors (NO_3^- , SO_4^{2-}) are relatively well-balanced at all sampling sites. The determination of evaluated trace elements in atmospheric deposition, Pearson's cross-correlation analysis, enrichment factor (EF) and seasonal variation showed a significant effect of the copper smeltery on the deposition flow quantity of zinc, lead and cadmium. Iron, aluminium, manganese and chromium have mainly source in a soil horizon and their deposition is significantly higher in the summer season. The elements in order Al, Fe, Cr, As, Pb and Mn were fixed mainly in the insoluble phase. Zinc, cadmium and a lesser extent of copper were predominant bound in soluble phase. The high values of deposition fluxes of cadmium (0.6–4.8), zinc (85.6–517.6), copper (24.1–159.2) and lead (9.0–116.7 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$) were detected in comparison with different regions. The highest values of these elements deposition fluxes were detected on sampling sites up to 3 km from copper smeltery.

Keywords: atmospheric deposition fluxes, copper smeltery, heavy metals, major ions

Introduction

The content of hazardous substances in atmospheric deposition (AD) significantly contributes to the pollution of environment. A study of qualitative and quantitative composition of AD provides important information for the assessment of air and environment quality. For this reason, many research studies deal with AD from viewpoint of various parameters and aspects (Azimi et al., 2005; Davis and Birch, 2011; Golomb et al., 1997; Hančulák et al., 2005; Nicholson et al., 2008). In industry areas, the content of AD is mainly formed by emissions from energetic and technological combustion processes. After sedimentation, the AD components interact with soil and other constituents of environment and in such way directly affect their quality. The specific composition of emissions from the technologies of metallurgy influences on constitution of atmospheric deposition, especially in the areas near this works. The main emission source in the area of Krompachy is the copper smeltery. The research was carried out in the area of the emission source and presents results from October 2009 to October 2013, predominantly from the viewpoint of influence of the works on deposition fluxes of selected trace elements (Fe, Al, Mn, Zn, Pb, Cu, Cr, Cd, As) and major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , SO_4^{2-} , NO_3^- , Cl^- , F^-).

Characteristics of the Krompachy area

The investigated area lies in the eastern part of Slova-

kia. It is situated in the Hornád river valley at 350 – 450 metres above sea-level. The elevation of the surrounding mountains reaches 1000 to 1100 m, a general orientation is east – west. The wind conditions are subject to the orography of the valley, which is relatively little wind, with frequent inverse conditions. In the area has been monitored a high 58% incidence of calms. The winds are dominated from the western and eastern directions, with a low average speed of 1 ms^{-1} . The wind speeds up to 2 ms^{-1} were observed in 25% of cases and the winds over 8 ms^{-1} were not observed (MŽP SR, 2009). In the copper smeltery, there are pyrometallurgically processed different types of copper-based waste namely brass, bronze and bimetal Fe-Cu, bimetal scrap there. Moreover, technological by-products such as copper slag, dross, filter sludge, cakes and other waste with copper content above 5% are also added to feed. The pyrometallurgical technology includes: copper blast furnace as a main source of emissions, converters and anode furnace. The final product is anode copper and copper wires. The secondary products of pyrometallurgy and collected dusts are processed hydrometallurgically to zinc sulphate heptahydrate. The total emissions of solid pollutants (SP) with a significant content of heavy metals were 29, 16 and 10 tons in the years 2010–2012.

The minor sources of SP in the monitored area are also foundry and two local boilers for the production of heat. Their SP emissions attain about 1 ton per year. The cop-

per smeltery also produces gaseous emissions, i.e. about 90 tons SO₂ and 40 tons NO_x per year. The whole area of the Central Spiš is well-known as a long-term loaded due to historical mining and follow metallurgical activities.

Materials and methods

Total atmospheric deposition i.e. the both wet and dry ones, were collected monthly from seven sites in the area of Krompachy from October 2009 to October 2013. The four open polyethylene cylinders (inside diameter – 12.5 cm and 16 cm height) with total sedimentation surface 490 cm² fitted on a stand were used for sampling. The four sites were localised on a periphery of the villages away from small local emission sources and roads, at about 2.5 m above the ground: 1MA – distance 10 km from the main source of emissions (chimney of the copper smeltery) 2SH – 5.5 km, 4KR – 1.2 km and 6KA – 1.4 km. The stands of the sites 3KL, 7SV and 5KO were located on the roofs buildings at about 3 and 15 m above ground, respectively. The distance from the main emission source was 4, 6 and 2.4 km.

The localization of sampling stations is illustrated in Fig. 1. The containers were filled with 200 ml of pure de-ionized 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 after 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). Consequently, the samples were mineralised by a microwave digestion MWS –3 Berghof. The trace metals were analysed by the atomic absorption spectroscopy using the device VARIAN with accessories: Fast Sequential AAS AA240 FS with Programmable Sample Dispenser PSD 120, GTA 120 and VGA-77 and by ICP- MS Agilent 7700. The analyses of major ions were performed by ion chromatography using Dionex ICS 5000. The average daily deposition fluxes per unit area by observed elements and ions were calculated on the basis mass of the obtained analyte and chemical analyses for each of the sampling sites. Enrichment factor (EF) was used to estimate whether the source of the trace elements in atmospheric deposition is of anthropogenic or natural origin. The reference element was aluminium. The EF was calculated as follows: $EF = (x/Al)_{\text{sample}} / (x/Al)_{\text{crust}}$.

The average amounts of the elements in crust are found in Mason (1966).

Results and discussion

Table 1 presents the average daily fluxes (μg.m⁻².day⁻¹) of trace elements and major ions except site 7SV during the monitored period September 2009 – October 2013. The samples from site 7SV have been analyzed from October 2011. The fluxes mainly of ions which have origin in gaseous precursors (NO₃⁻, SO₄²⁻) are well-balanced at all sampling sites. Partly larger differences for the deposition of ions K, Ca and Mg were found on the sites 5KA, 1MA and 7SV. The sources of these ions are particles coming from the soil horizon and nearby limestone quarries. The effect of the copper smeltery emissions on the deposition of observed major ions were not recorded as opposed to the deposition of trace elements whose origin is clearly in operation of the copper smeltery. Among various sampling sites high differences in the deposition were determined mainly for Zinc, lead, copper and cadmium. The highest values of these metals, arsenic and partially chromium were measured in the sampling sites localized in vicinity of the copper smeltery, i.e. 4KR, 6KO and 5KA, in the distance of 1.2 km, 2.4 km and 1.4 km respectively. The lowest values of these metals were detected at a sampling site 1MA, that is furthest from the copper smeltery in the distance 10 km. There were not so high differences in the deposition of iron, aluminium and manganese.

The deposition fluxes of the elements from the area were compared with results from other areas such as rural areas in Czech Republic, England, Wales, Austria and USA, urban and suburban areas in Serbia, France and China (Hančulák et al., 2012; 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). In the area of Krompachy, the deposition fluxes of Cd, Cu, Zn and Pb exceeded the corresponding data from these studies, especially at sites localized in the immediate vicinity of the copper smeltery (4KR, 6KO, 5KA).

Figure 2 shows the average deposition fluxes of observed trace elements and their presence in the winter and summer period. As to Fe, Al, Mn, Cr and As a significantly higher presence in the summer period was showed. The ratio between their deposition in summer and winter was 2.2, 3.5, 3.0, 1.9 and 2.9 respectively. The origin of these

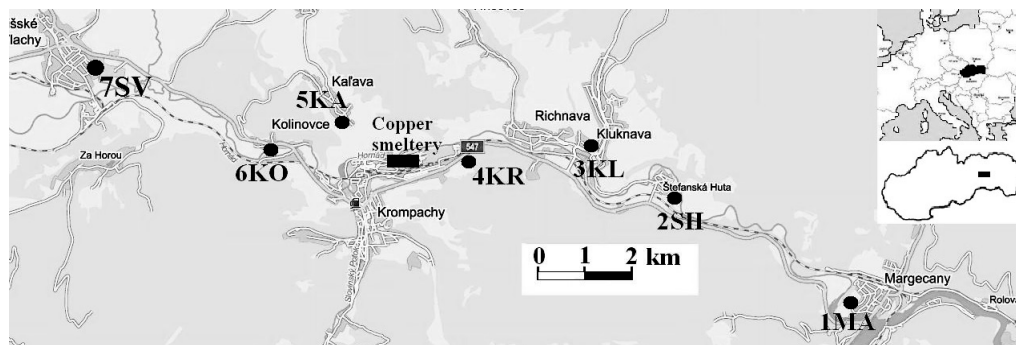


Fig. 1 Location of the sampling sites and the copper smeltery

Rys. 1 Lokalizacja miejsc pobierania próbek oraz huta miedzi

Tab. 1 The average daily bulk deposition fluxes of trace elements and major ions [$\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$]

Tab. 1 Średnie dzienne osadzanie się strumieni pierwiastków śladowych oraz najważniejszych jonów [$\mu\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$]

Site	Fe	Al	Mn	Zn	Pb	Cu	Cr	Cd	As
1MA	544	869	21.9	85.6	9.01	24.06	2.84	0.56	0.48
2SH	597	544	14.5	140.4	17.39	29.35	4.01	1.06	0.46
3KL	679	540	12.4	174.5	23.65	41.95	3.17	1.07	0.52
4KR	560	455	18.8	517.6	116.66	159.23	3.54	4.76	1.76
5KA	378	476	15.2	132.3	12.32	40.26	3.55	1.39	2.25
6KO	655	589	17.1	293.2	64.73	101.34	4.34	2.54	1.23
7SV	1358	1467	29.2	147.0	18.13	21.84	5.13	0.33	1.43
Aver. (n=52)	640	670	18.2	218.6	38.51	62.65	3.73	1.76	1.20
Median	601	540	14.7	131.2	17.72	36.78	3.04	0.84	0.66
Site	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	F ⁻
1MA	2417	303	474	1146	1011	4748	1927	1016	132
2SH	1717	268	419	589	810	3174	2096	826	99
3KL	1355	185	272	343	792	3148	2101	593	97
4KR	1704	234	381	842	956	3256	1871	892	164
5KA	1455	221	385	1741	1352	3535	1665	1162	103
6KO	1622	210	293	378	878	3016	1990	662	160
7SV	2891	360	454	431	1088	3079	1705	721	99
Aver. (n=118)	1875	254	382	760	979	3424	1912	837	122
Median	1427	188	350	466	736	3102	2005	734	98

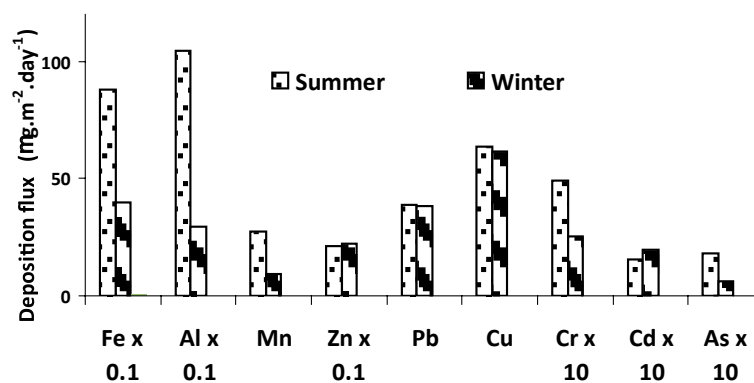


Fig. 2 Seasonal variation of deposition fluxes trace elements (average from all sampling sites)

Rys. 2 Sezonowe zróżnicowanie osadzania się strumieni pierwiastków śladowych (średnia ze wszystkich miejsc pobierania próbek)

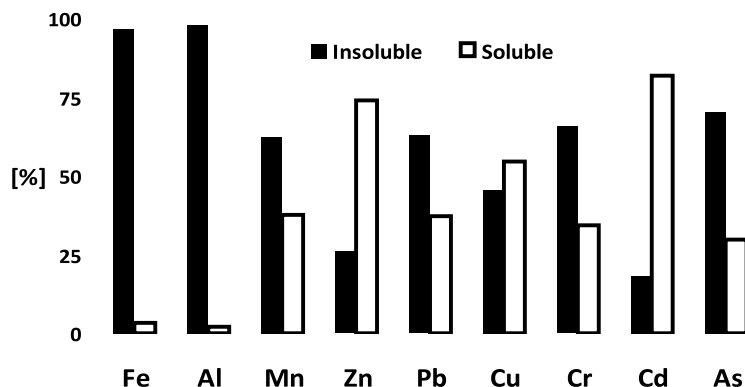


Fig. 3 The average element abundances in soluble and insoluble phase [%].

Rys. 3 Średnia ilość pierwiastków w fazie rozpuszczalnej i nierozpuszczalnej [%]

elements indicates their sources mainly in the soil horizon. Probably, there are better conditions for re-suspension and remote transport of particles containing these elements during summer period. In the case of elements which come predominantly from copper smeltery relatively balanced values were recorded for both seasons. The ratio was 0.78, 1.03, 0.96 and 1.02 for the deposition fluxes of Cd, Cu, Zn and Pb, respectively.

Figure 3 shows the average element abundances of studied metals in "water soluble" and "insoluble" phase. The metals in order Al, Fe, Cr, As Pb and Mn (on average slightly more than 50%) were fixed mainly in the insoluble phase. The zinc, cadmium and a lesser extent of the copper were predominant bound in soluble phase.

The statistical dependence among deposition of observed elements were evaluated by Pearson's correlation analysis. The Pearson's cross-correlation coefficients are summarized in Table 2. The high positive values of the correlation coefficient were calculated for two relatively independent groups of elements. In the first group higher values among elements Fe, Mn, Al, and Cr ($r = 0.58$ to 0.79) were found. In the second group among elements Zn, Cd, Pb and Cu, the values of the correlation coefficient r were in the range $0.61 - 0.90$. Besides of these two groups an occurrence of arsenic has its specificity. It attains relatively high correlation coefficient values in the case of As/Pb $r = 0.54$, As/Cu $r = 0.66$, $As/Mn = 0.61$, $As/Fe = 0.50$, lower

in the case of As/Al $r = 0.41$, As/Zn $r = 0.34$ and $As/Cd = 0.23$. Thus, particles from contaminated soil horizon due to historical mining and metallurgical activities can also be a source of arsenic in the area of Krompachy.

Enrichment factor (EF) analysis was used to investigate the relative contribution of anthropogenic and natural sources on the atmospheric deposition fluxes of studied metals. The EF values closely 1 point to the fact that the source of these elements is mostly crustal erosion while elements with EF values larger than about 4 have some other source. According to the degree of enrichment, the elements can be considered as highly enriched ($EF > 100$), intermediately enriched ($10 < EF < 100$) and less enriched ($EF < 10$) (Kyllonen et al., 2009; Mijić et al., 2011). The EF values for the elements calculated from the average total deposition at the all sampling sites and whole period are shown in Fig. 4.

The high and intermediately EF values for Zn (108 – 1243), Pb (61 – 1500), Cu (33 – 422), As (30 – 211) and Cd (5 – 78) were detected for all sampling sites, except two cases for Cd (1MA, 7SV). The highest values of EF for these metals were found at the sampling sites in vicinity of the copper smeltery, i.e. 4KR, 6KR and 5KR. Conversely, the lowest values were detected at the farthest site 1MA. This fact confirms the significant effect of the copper smeltery on AD of these metals in its vicinity. The EF values for Fe, Al, Mn and a lesser extent in the case of Cr indicated the

Tab. 2 The Pearson's cross-correlation coefficients between fluxes of trace elements.

Tab. 2 Korelacja krzyżowa współczynników Pearsona pomiędzy strumieniami pierwiastków śladowych

	Al	Mn	Zn	Pb	Cu	Cr	Cd	As
Fe	0.78	0.79	-0.07	0.02	-0.01	0.60	-0.18	0.50
Al	-	0.78	-0.18	-0.13	-0.16	0.46	-0.27	0.41
Mn	0.78	-	-0.03	0.03	0.06	0.58	-0.15	0.61
Zn	-0.18	-0.03	-	0.61	0.78	0.05	0.90	0.34
Pb	-0.13	0.03	0.61	-	0.88	-0.02	0.67	0.54
Cu	-0.16	0.06	0.78	0.88	-	0.08	0.85	0.57
Cr	0.46	0.58	0.05	-0.02	0.08	-	0.03	0.39
Cd	-0.27	-0.15	0.90	0.67	0.85	0.03	-	0.23
As	0.41	0.61	0.34	0.54	0.57	0.39	0.23	-

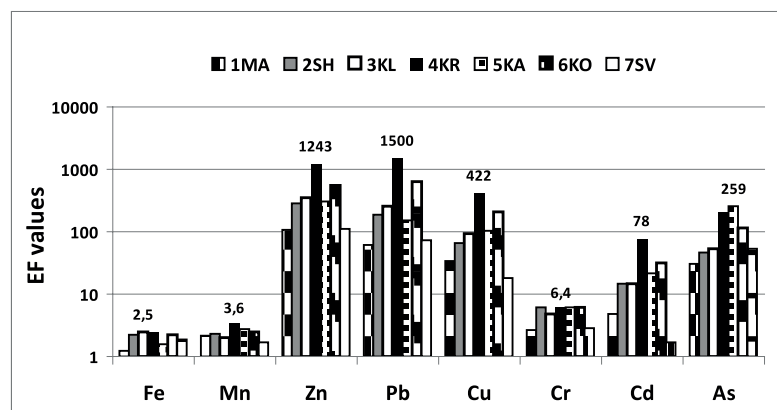


Fig. 4 The average values of enrichment factor (EF) for individual sampling sites

Rys. 4 Średnia wartość współczynnika wzbogacenia (EF) dla pojedynczego miejsca pobrania próbek

nature origin of these elements mainly from soil horizon.

Conclusion

The atmospheric bulk deposition, its qualitative and quantitative characteristics were studied by deposition fluxes of major ions and trace elements from 7 sampling sites in the area of Krompachy in vicinity copper smeltery. An influence of the copper smeltery emissions on the deposition by major ions was not recorded. On the other hand the deposition of trace elements is clearly effected by the copper smeltery operation. The determination of evaluated trace elements in AD deposition, correlation analysis, enrichment factor (EF) and seasonal variation showed a significant effect of the works on the deposition flow quantity

of Zn, Pb, Cu, Cd and lesser extent of As. The metals such as Fe, Al, Mn, Cr have their source mainly in a soil horizon and their deposition is significantly higher in the summer season. The high values of deposition fluxes of cadmium, zinc, copper and lead were detected in comparison with different regions. The highest values of these elements deposition fluxes were detected on sampling sites up to 3 km from copper smeltery.

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Wpływ huty miedzi w Krompachach (Słowacja) na depozycję atmosferyczną

Próbki opadów atmosferycznych, zarówno mokrych i suchych, zebrano w obszarze Krompachy w pobliżu huty miedzi w latach 2009 – 2013. Pobieranie próbek wykonywane było w siedmiu miejscach położonych od 1,2 do 10 km od głównego źródła zanieczyszczenia. Oznaczone były jony główne (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , SO_4^{2-} , NO_3^- , Cl^- , F^-) i pierwiastki śladowe (Fe, Al, Mn, Zn, Pb, Cu, Cr, Cd, As). Strumienie pierwiastków śladowych w depozytach atmosferycznych zostały określone odrębnie dla fazy "rozpuszczalnej w wodzie" i "nierozpuszczalnej". Wpływ odległości miejsc pobierania próbek od huty miedzi na absolutne wartości zawartości jonów głównych nie były rejestrowane. Z drugiej strony osadzanie pierwiastków śladowych jest wyraźnie efektem działań huty miedzi. Strumienie jonów, które mają źródło w prekursorach gazowych (NO_3^- , SO_4^{2-}) są stosunkowo dobrze zrównoważone na wszystkich miejscach pobierania próbek. Określenie ocenianych pierwiastków śladowych w depozycji atmosferycznej, korelacja krzyżowa analizy Pearsona, współczynnik wzbo-gacenia i sezonowe wahania wskazują na znaczący wpływ huty miedzi na ilość osadzanego cynku, ołowiu i kadmu. Żelazo, aluminium, mangan i chrom mają źródło głównie w glebie i ich osadzanie jest znacznie wyższe w sezonie letnim. Pierwiastki w kolejności Al, Fe, Cr, As, Pb i Mn były związane głównie w fazie nierozpuszczalnej. Cynk, kadm i w mniejszym stopniu miedź były przeważnie związane w fazie rozpuszczalnej. Wysokie wartości strumieni osadzania kadmu (0,6 - 4,8), cynku (85,6 - 517,6), miedzi (24,1 - 159,2) i ołowiu (9,0-116,7 $\mu g \cdot m^{-2} \cdot dzień^{-1}$) zostały wykryte w porównaniu z innymi regionami. Najwyższe wartości strumieni depozycji tych pierwiastków zostały wykryte w miejscach pobierania próbek do 3 km od huty miedzi.

Słowa kluczowe: strumienie osadów atmosferycznych, huta miedzi, metale ciężkie, główne jony