Abstract

The contribution deals with the atmospheric deposition of solid particles and selected elements in the typical urban area with many sources of pollution. The main sources of pollution are represented by neighboring the iron and steel works and the thermal power station. The samples were collected from the eleven sites, which are located from 3.6 to 16 km from the iron and steel works. 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 and their seasonal variations were studied. Results from the years of 2009–2018 are introduced. The research has shown a significant influence of local sources of pollution on the studied parameters of atmospheric deposition. Compared to the values of deposition measured in the other areas, extremely high values of iron (28, 120), manganese (1,106) and chromium (34.1 μg.m⁻².day⁻¹) deposition as well as high, above-average values of other monitored elements were measured in the proximity of the ironworks. The portion of emission sources of iron and steel works on the Fe fluxes at the individual sites in the city was calculated in the range from 24.7 to 54.1%. On the basis of the emission situation of the monitored area, it is possible to use selected compounds of the AD as an environment quality indicator and to quantify the contribution of emissions to area's environmental stress.

Keywords: atmospheric deposition, emissions, iron and steel works, metals

Introduction

Atmospheric deposition (AD) is a significant source of many pollutants and their major input into the surface and other components of an environment. Specific anthropogenic emissions from the large sources of pollution have influence on the composition of 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 provides important information for an assessment of air and environment quality. For this reason, many research studies deal with AD from point of view of various parameters and aspects in urban, suburban and rural areas (Azimi et al., 2005; Hančuľák et al., 2011, 2015, 2016; Kara, M. et. al., 2014; Mehrazin et al., 2017, Putaud et al., 2010, 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 environmentally loaded by the iron and steel works – the largest source of emissions of various pollutants including particulate matter and metals. Metals are regarded as very good markers of the specific natural and anthropogenic pollution sources, to a large extent they are used in studies dealing with determination and division of sources of solid particles (Nicolač et. al., 2007). The contribution presents some results of the research of AD which was conducted by the bulk deposition methodology from 2009 to 2018 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 the iron and steel works.

Characteristics of the area

The monitored area is located in the Košice Basin, in the valley of the river Hornád with north-south orientation in the eastern part of Slovakia. The prevailing winds in the area are northern (53.5%) and southern (31.6%), while the proportion of calm is 9.5%. Emissions of particulate matter (PM) have the greatest influence on its composition in terms of monitored components of AD. The decisive producer of particulate matter (PM) and gaseous emissions in the area of Košice, as well as the whole Slovakia is the iron and steel industry complex, the company U. S. Steel Košice, Ltd., located approx. 10 km south to southwest of the city center. Limekiln (Carmeuse Slovakia, Ltd.) and several other metallurgical companies are placed directly in the industrial estate of works. Directly, in the southern part of the city, a heating plant (TEKO) is located that produces heat and electricity based on coal and natural gas. Inventory emissions of PM and selected metals from crucial sources of pollution in the area are processed in Table 1 and Table 2 (NEIS).

Materials and methods

Total atmospheric deposition i.e. both wet and dry ones, were collected monthly (35 ± 5 days) from eleven sites in the urban and suburban area in the vicinity of iron and steel works, from June 2009 to October 2018. 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.

In the urban area, the sites no. 1–6 were placed on the rooftops of blocks of flats and public buildings at 24–36 m height above the ground level, above the height of surroundings.
ing buildings, 4–12 m in the case of suburban and rural sites no. 7–11. The four open polyethylene cylinders (inside diameter – 12.5 cm) filled with 200 ml of pure deionized water fitted on a stand were used for sampling. In laboratory the contents of cylinders were filtered by a vacuum filtration through 0.40 µm membrane filters to separate the “water soluble” and “insoluble” fractions (PM). The soluble fraction was analyzed after each sampling. The insoluble fraction designated for analysis was prepared by cumulation of six monthly samples into the one semi-annual sample – summer and winter period (mid-April – mid-October) and by mineralization using a microwave digestion. The elements were analyzed by the atomic absorption spectroscopy using the device VARIAN AA240 FS with GTA 120 and VGA-77. Since October 2012, the device ICP MS Agilent 7700 has been used for analysis. In the article, the results of 10 summer and 9 winter periods from 2009 to 2018 are processed.

Results and discussion

Table 3 presents the average daily fluxes (µg.m⁻².day⁻¹) of observed elements and solid particles – PM (“water insoluble” part of AD) from total bulk deposition and basic statistic parameters for all sampling sites and the whole monitored period (September 2009 – October 2018). Absolute values of deposition of observed elements and PM from sites north of ironworks are relatively balanced, without increased values at site No.5. The site is located in the city center with heavy traffic and high construction activities during monitored period, about 2 km northward of the thermal power station, which used coal apart from gas as fuel mainly in heating season. The maximum values of all studied metals and PM 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 2.2 to 16.5 (Fe = 8.4, Al = 3.9, Mn = 16.5, Zn = 2.5, Pb = 5.2, Cu = 4.3, Cr = 6.3, Cd = 2.2 and As = 2.3).

In the table 4 is shown the average percentage representation of the deposition of trace elements bound to the “water-insoluble” (PM) part of AD and the ratio between summer and winter atmospheric deposition of the monitored elements and PM. To the insoluble phase, the monitored elements in order of Al, Fe, Mn Cr, Pb and As are bounded. Cd and Zn are preferentially bounded to the soluble phase for sites north of ironworks. 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.

Deposition of particulate matter and aluminum is significantly higher in summer period (ratio S/W - 0.55 and 0.60). There are better conditions for wind erosion and resuspension of particles from soil horizon, road traffic, agricultural and construction activities as well as the increased presence of organic detritus in the air in summer period. In winter, the deposition fluxes of solid particles are partially deprived of these effects. In winter seasons increased amount of components of AD, whose origin is in energy burning of fossil fuels on local and regional scale is assumed. In the area of Košice, slightly higher or balanced values of deposition fluxes in the order Pb, Cr, Fe, Mn, Cu and Cd (R_S/ W = 1.21 -1.00) were found in winter. In the case of zinc (R_S/W = 0.79) and arsenic (R_S/W = 0.63) the higher values were recorded in the summer period. The smallest seasonal differences for all observed components were detected at sites near the ironworks (No. 9 and 10) and the station No. 5.

The relationship between the deposition of the observed elements and PM from all measured period and the distance from the iron and steel works was studied by regression analysis. The results are graphically presented in the figure 2. The significant dependence was found in descending order for the Pb, Cr, Fe, Mn, Cu and Cd (R_S/W = 1.21 -1.00) were found in winter. In the case of zinc (R_S/W = 0.79) and arsenic (R_S/W = 0.63) the higher values were recorded in the summer period. The smallest seasonal differences for all observed components were detected at sites near the ironworks (No. 9 and 10) and the station No. 5.

The statistical dependence between individual atmospheric deposition of observed metals and PM was evaluated by Pearson’s correlation analysis. The Pearson’s cross-correlation coefficients are summarized in the Table 5. The highest values of correlation coefficients (r = 0.82 to 0.94) were calculated between elements where their dominant source are technologies of ironworks, namely Mn, Fe and Cr. The high values of the correlation coefficients were calculated for these
Tab. 3. The average daily fluxes of atmospheric deposition of particles (PM – insoluble fraction) and analyzed elements from 10 summer and 9 winter monitored periods (April 2009 – October 2018), [μg.m⁻².day⁻¹] (* – Finished April 2014, ** – Finished April 2017, # – Start sampling October 2011)

| Site | PM (μg.m⁻².day⁻¹) | Fe (μg.m⁻².day⁻¹) | Al (μg.m⁻².day⁻¹) | Mn (μg.m⁻².day⁻¹) | Zn (μg.m⁻².day⁻¹) | Pb (μg.m⁻².day⁻¹) | Cu (μg.m⁻².day⁻¹) | Cr (μg.m⁻².day⁻¹) | Cd (μg.m⁻².day⁻¹) | As (μg.m⁻².day⁻¹) |
|------|-------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| 1    | 37187             | 2970             | 1166             | 63               | 83               | 231              | 11.7             | 5.5              | 0.34             | 1.11             |
| 2    | 38290             | 3070             | 1315             | 62               | 69               | 24.8             | 10.1             | 5.9              | 0.26             | 1.24             |
| 3**  | 43916             | 2933             | 1039             | 60               | 87               | 19.9             | 8.7              | 5.4              | 0.40             | 0.87             |
| 4*   | 38840             | 3432             | 1007             | 64               | 83               | 9.8              | 9.3              | 4.8              | 0.27             | 1.14             |
| 5*   | 83969             | 5214             | 1751             | 96               | 112              | 14.4             | 17.3             | 8.6              | 0.34             | 1.26             |
| 6*   | 39199             | 2797             | 870              | 53               | 67               | 7.6              | 8.5              | 4.8              | 0.22             | 0.51             |
| 7    | 44318             | 5029             | 1288             | 92               | 102              | 39.2             | 11.2             | 6.2              | 0.32             | 1.37             |
| 8**  | 31201             | 3265             | 1031             | 75               | 116              | 23.9             | 9.0              | 5.2              | 0.28             | 0.74             |
| 9#   | 163694            | 28120            | 4110             | 1106             | 219              | 110.7            | 42.3             | 34.1             | 0.65             | 3.63             |
| 10#  | 129124            | 21206            | 3303             | 652              | 207              | 105.0            | 19.6             | 18.3             | 0.66             | 2.47             |
| 11#  | 49402             | 4438             | 1473             | 79               | 93               | 28.5             | 13.0             | 4.7              | 0.19             | 1.50             |
| Average (n = 166) | 60331            | 7131             | 1661             | 211              | 113              | 9.2              | 16.0             | 9.2              | 0.36             | 1.45             |
| Min. | 11019             | 1097             | 173              | 19               | 35               | 0.3              | 0.9              | 0.3              | 0.04             | 0.02             |
| Max. | 264981            | 34032            | 6922             | 1905             | 695              | 63.4             | 404.1            | 63.4             | 3.01             | 13.01            |
| Median | 45351             | 3528             | 1711             | 72               | 84               | 5.6              | 10.9             | 5.6              | 0.26             | 1.06             |

The deposition fluxes of the elements from the area of Košice were compared with results from different urban and suburban areas (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 this comparison, above average deposition of Fe, Mn and Cr, partially in the case of Zn was detected. The most significant differences were found for the deposition of iron and manganese. 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 site No. 9, deposition of Fe and Mn was 15 or 38 times higher, deposition of Cr 2.5 or 6 times higher. The site is located approximately 1 km from the iron works area and their, almost 100% effect on Fe deposition can be assumed, which is fixed almost only to PM in AD. The calculated impact of resources of ironworks on the deposition of Fe at other sites in the area was built on this fact. The average percentage of Fe deposition from PM at site No. 9 was taken as the basis 100% (B100%) after deduction of regional background (AD<sub>Fe Background</sub>) of iron deposition: B100 % = (AD<sub>Fe Site No.9</sub> - AD<sub>Fe Background</sub>) / (AD<sub>PM Site No.9</sub> / 100).

The corresponding values from the other sites were compared with the result of this calculation.

The average value of iron deposition from the area Krompachy (7 sites) obtained by using the same methodology was used as a background (AD<sub>Fe Background</sub> = 600 μg.m⁻².day⁻¹) [12]. Calculating contemplated with 2 x AD<sub>Fe Background</sub> = 1200 μg.m⁻².day⁻¹ for sites in the city (No. 1–8) due to the impact of other sources of emissions in urban environment. Iron in the Fe₂O₃ form was taken in the calculation for correction of PM deposition. In the table 5 the calculated average percentage proportion of emission sources from iron and steel works on the AD of Fe fluxes at the individual sites is shown.

The portion of emission sources of iron and steel works on the Fe fluxes at the individual sites in the city was calculated in the range from 24.7 to 54.1%. The portion decreases proportionally with increasing distance as illustrated in Figure 3.
Tab. 4. The average element abundances in insoluble fraction (PM) [%] and the ratio between winter and summer atmospheric deposition of the observed elements and PM

| Element | PM | Fe | Al | Mn | Zn | Pb | Cu | Cr | Cd | As |
|---------|----|----|----|----|----|----|----|----|----|----|
| Element abundances [%] | -  | 96 | 97 | 58 | 23 | 58 | 42 | 71 | 24 | 65 |
| Ratio between ADw/ADs | 0.55 | 0.60 | 1.20 | 1.12 | 0.79 | 1.21 | 1.00 | 1.21 | 1.00 | 0.63 |

Fig. 2. The dependence between the deposition of the PM and observed elements and the distance from the iron and steel works U.S. Stel, Ltd.

Rys. 2. Zależność między osadzaniem się PM a obserwowanymi pierwiastkami oraz odległością od huty żelaza i stali U.S. Stel, Ltd.
The lowest portion was found at the furthest station No. 3, the highest portions at the sites located closest to the ironworks. With respect to composition of emissions from ironworks, the iron is their major component and also of AD of PM. It can be assumed that this specified proportion of the ironworks sources on deposition is not valid only for Fe but also for PM and other components fixed mainly to particles produced from these sources.

**Conclusion**

A detailed analysis of the atmospheric deposition of studied metals and solid particles proved a decisive influence of emissions from the ironworks on the composition of AD in the monitored area.Comparatively high seasonal and spatial variability of deposition of monitored elements and solid particles was detected on a relatively small area in urban and suburban environment. The proportion of the ironworks sources of environmental burden on a monitored area was quantified based on the iron deposition. Compared to the values of deposition measured in the other areas, extremely high values of iron, manganese and chromium deposition as well as high, above-average values of other monitored elements were measured in the proximity of the ironworks. On the basis of the emission situation of the monitored area, it is possible to use selected compounds of the AD as an environment quality indicator and to quantify the contribution of emissions to area’s environmental stress.

**Acknowledgment**

The authors are grateful to the Slovak Grant Agency for Science (Grant No. 2/0165/19) for financial support of the work.

| Site | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    | 10   | 11   |
|------|------|------|------|------|------|------|------|------|------|------|------|
| Distance from iron works (km) | 13.4  | 10.7 | 16.3 | 15.1 | 12.3 | 10.4 | 8.6  | 8.5  | 3.6  | 5.5  | 9.0  |
| The average percentage portion (%) | 30.0  | 30.8 | 24.7 | 36.2 | 29.4 | 32.9 | 54.1 | 42.1 | 100.0| 94.5 | 40.8 |

Fig. 3. The portion of emission sources of iron and steel works on the Fe deposition fluxes in depending on the distance sampling sites from sources of iron and steel works

Rys. 3. Emisja z hut żelaza i stali w zależności od odległości miejsc pobierania próbek od źródeł huty żelaza i stali

Tab. 5. The Pearson’s cross-correlation coefficients between fluxes of trace elements (n = 166)

|       | Fe  | Al  | Mn  | Zn  | Pb  | Cu  | Cr  | Cd  | As  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| PM    | 0.84| 0.84| 0.82| 0.57| 0.44| 0.51| 0.73| 0.44| 0.51|
| Fe    | 0.82| 0.94| 0.52| 0.68| 0.44| 0.82| 0.45| 0.55|     |
| Al    | 0.82| 0.78| 0.47| 0.48| 0.36| 0.70| 0.34| 0.49|     |
| Mn    | 0.94| 0.78| 0.53| 0.55| 0.48| 0.91| 0.49| 0.45|     |
| Zn    | 0.52| 0.47| 0.53| 0.33| 0.30| 0.50| 0.56| 0.32|     |
| Pb    | 0.68| 0.48| 0.55| 0.33| 0.17| 0.39| 0.47| 0.57|     |
| Cu    | 0.44| 0.36| 0.48| 0.30| 0.17| 0.54| 0.43| 0.36|     |
| Cr    | 0.82| 0.70| 0.91| 0.50| 0.39| 0.54| 0.43| 0.35|     |
| Cd    | 0.45| 0.34| 0.49| 0.56| 0.47| 0.43| 0.43| 0.36|     |
| As    | 0.55| 0.49| 0.45| 0.32| 0.57| 0.36| 0.35| 0.36|     |

Tab. 6. The average percentage portion of emission sources of iron and steel works on the Fe deposition fluxes at the individual sites

| Site | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 10    | 11    |
|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Distance from iron works (km) | 13.4  | 10.7  | 16.3  | 15.1  | 12.3  | 10.4  | 8.6   | 8.5   | 3.6   | 5.5   | 9.0   |
| The average percentage portion (%) | 30.0  | 30.8  | 24.7  | 36.2  | 29.4  | 32.9  | 54.1  | 42.1  | 100.0 | 94.5  | 40.8  |

y = 377.7x^{-0.9758}

R² = 0.8647
Artykuł dotyczy emisji do powietrza cząstek stałych i wybranych pierwiastków w typowym obszarze miejskim z wieloma źródłami zanieczyszczeń. Głównymi źródłami zanieczyszczeń są sąsiednie huty żelaza i stali oraz elektrownia cieplna. Próbki pobrano z jedenaściu stu miejsc, które znajdują się w odległości od 3,6 do 16 km od huty żelaza i stali. Badano cechy ilościowe i jakościowe całkowitej emisji cząstek stałych, strumienie osadzania pierwiastków Fe, Al, Mn, Zn, Pb, Cu, Cr, Cd, As oraz ich sezonowe zmiany. Przedstawiono wyniki z lat 2009–2018. Badania wykazały znaczący wpływ lokalnych źródeł zanieczyszczeń na badane parametry zanieczyszczeń w atmosferze. W porównaniu z wartościami depozycji zmierzonymi w innych obszarach, wyjątkowo wysokie wartości zawartości żelaza (28, 120), manganu (1106) i chromu (34,1 μg.m⁻².dni⁻¹), a także wysokie, ponadprzeciętne wartości innych monitorowanych pierwiastków zmierzono w poblizu huty. Część źródeł emisji hut żelaza i stali w poszczególnych lokalizacjach w mieście stwierdzono w przedziale od 24,7 do 54,1%. Na podstawie sytuacji emisyjnej monitorowanego obszaru można zastosować wybrane związki AD jako wskaźnik jakości środowiska i określić ilościowo udział emisji w obciążeniu środowiskowym obszaru.

Słowa kluczowe: emisja do atmosfery, emisja, huty żelaza i stali, metale

Literatura – References

1. AZIMI, S.; ROCHER, V.; GARAUDA, S.; VARRAULT, G.; THEVENOT, D.R. Decrease of atmospheric deposition of heavy metals in an urban area from 1994 to 2002. Chemosphere. 2005, No. 6, p. 645-651. ISSN 0045-6535.
2. HANČULÁK, J., FEDOROVÁ, E., ŠESTINOVÁ, O., ŠPALDÓN, T., MATIK, M. Influence of iron ore works in Nižná Slaná on atmospheric deposition of heavy metals. In Acta Montanistica Slovaca, 16, 2011, p. 220-228. ISSN 1335-1788.
3. HANČULÁK, J. et al. Atmospheric Deposition of Solid Particles in the Area of Košice. Solid State Phenomena, 2016, vol. 244, p. 188-196.
4. HANČULÁK, J. et al.: Influence of Iron and Steel Industry on Selected Elements of Atmospheric Deposition in the Urban and Suburban Area of Košice (Slovakia). In Inżynieria Mineralna – Journal of the Polish Mineral Engineering Society, 2015, vol. 16, no. 2, p.95-102.
5. KARA, M. et. al. Seasonal and spatial variations of atmospheric trace elemental deposition in the position of the industrial region, Turkey. In: Atmos. Res.149 (2014) 204–216.
6. MIJić, Z., STOJIĆ, A., PERIŠIĆ, M., RAJŠIĆ, S., TASIĆ, M., RADENKOVIĆ, M., JOKSIĆ, J. Seasonal variability and source apportionment of metals in the atmospheric deposition in Belgrade. Atmospheric Environment, 44,3, 2010, 3630-3637.
7. MEHRAZIN, O., RUBAN, V., RUBAN, G., LAMPREA, K. Assessment of atmospheric trace metal deposition in urban environments using direct and indirect measurement methodology and contributions from wet and dry depositions Atmospheric Environment, 168 (2017), 101-111.
8. NEIS (Národný emisný informačný systém) [online]. C2015 [cit. 2019-04-18]. Dostupné z WWW: <http://www.air.sk> (National Emission Information System of Slovak Republic)
9. NICOLÁS, J.F. et. al., 2008. Quantification of Saharan and local dust impact in an arid Mediterranean area by the positive matrix factorization (PMF) technique. Atmos. Environ. 42, 8872-8882.
10. NICHOLSON, F.A. et al. An inventory of heavy metals inputs to agricultural soils in England and Wales. Science of the Total Environment. 2003, Vol. 311, p. 205-219. ISSN 0048-9697.
11. PRÁŠKOVÁ, L.; KUBÍK, L.; MALÝ, S.: The control and extraneous matter monitoring in the farmlands and farm inputs. Annual report 2005. Central institute for supervising and testing in agriculture in Brno, 2006, p. 13.
12. PUTAUD, J.P. et al., 2010. A European aerosol phenomenology-3: physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. Atmos. Environ. 44, 1308-1320.
13. QUEROL, X. et. al. 2007. Source origin of trace elements in PM from regional background, urban and industrial sites of Spain. Atmos. Environ. 41, 7219-7231.
14. SPIEGEL, H., BÖHM K.E., ROTH K. SAGER, M. Atmospheric deposition of trace metals onto arable land in Austria. Proc. 7th Intern. Conf. On the Biogeochem. Of Trace Elements; Uppsala’03, 2003, p. 90.
15. WONG, C.S.C.; LI, X.D.; ZHANG, S.H.QI.; PENG, X.Z. Atmospheric deposition of heavy metals in the Pearl River Delta, China. Atmospheric Environment. 2003, Vol. 37, p. 767-776. ISSN 1352-2310.