# The Influence of Metallurgical Industry Emissions on the Development of Selected Components of Atmospheric Deposition in the Košice Area (Slovakia)

Jozef Hančuľák[1*)], Petra Červeňáková[2)], Oľga Šestinová[3)], Lenka Findoráková[4)]

[1*)] Institute of Geotechnics of Slovak Academy of Sciences, Watsonova 45, 04001 Košice, Slovakia; email: hanculak@saske.sk; https://orcid.org/0000-0002-0374-1555

[2)] Institute of Geotechnics of Slovak Academy of Sciences, Watsonova 45, 04001 Košice, Slovakia; email: cervenakova@saske.sk; https://orcid.org/0000-0001-6386-6969

[3)] Institute of Geotechnics of Slovak Academy of Sciences, Watsonova 45, 04001 Košice, Slovakia; email: sestinova@saske.sk; https://orcid.org/0000-0003-1684-7882

[4)] Institute of Geotechnics of Slovak Academy of Sciences, Watsonova 45, 04001 Košice, Slovakia; email: findorakova@saske.sk; https://orcid.org/0000-0002-2287-3596

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*Abstract*

*The aim of this paper is to assess the impact of emissions and their decrease on the level of environmental burden through the study of selected atmospheric deposition parameters in the area with the dominant source of emissions from the iron and steel production complex. Total atmospheric deposition (AD), i.e., j. both wet and dry, was sampled from eleven sampling points at a distance of 3 to 16 kilometers from the ironworks complex. AD fluxes of selected elements (Fe, Al, Mn, Zn, Pb, Cu, Cr, Cd, As) and dust particles (PM) were evaluated in relation to the amount of emissions from the results of long-term AD monitoring (2009 – 2022). The analysis shows the dominant influence of emissions from the metallurgical industry on the deposition fluxes of most of the monitored parameters and, thus, on the environmental burden of the area. The emissions have a decisive impact on the AD of manganese, iron, chromium, particulate matter, zinc, and aluminum, but also, to a lesser extent, on the AD of the other monitored elements. Correlation analysis confirmed a statistically significant dependence between the amount of emissions and the mass fluxes of AD for iron, zinc, manganese, and chromium for most of the sampling sites. The potential of immission load of the urban environment of Košice by emissions from the metallurgical industry is significantly higher in the winter due to local specific meteorological conditions. The more than sevenfold decrease in emissions significantly affected the AD of most of the monitored parameters, but their decrease was not so significant except for the AD of lead. The average AD of the elements strongly associated with ironworks emission sources, namely iron, manganese, chromium, and zinc, decreased approximately twofold. The amount of emissions is only one of several factors that affect the quantity of fluxes of the monitored AD parameters. In addition to seasonal factors, local meteorological, climatic, orographic, and other local conditions, and specifics also play an essential role.*

*Keywords: atmospheric deposition, emissions, metallurgy, metals*

**Introduction**

The Košice area, apart from the typical urban sources of pollution, has been exposed to the influence of the largest industrial source of emissions in Slovakia, which is the iron and steel production complex, U.S Steel Košice, Ltd., for a long time. It emits thousands of tonnes of gaseous and particulate emissions of a wide range of pollutants annually. Especially particulate matter (PM) in the air is considered a severe problem in terms of health and other environmental risks [1]. Atmospheric deposition processes transfer emissions from the air to other components of the environment. Specific particulate emissions from the metallurgical complex contain relatively high levels of metals and trace elements and significantly affect the qualitative and quantitative composition of atmospheric deposition (AD), particularly in its vicinity. Therefore, the research of atmospheric metal deposition fluxes and their interrelationships can be a helpful tool to identify the sources and origins of particulate matter. In air quality and environmental load assessments, metals and trace elements are often analyzed as pollutants alone but are also used as markers of specific anthropogenic and natural emission sources [2-6].

Research on total atmospheric deposition in the urban and nearby industrial environment in relation to the primary sources of particulate matter emissions in the Košice area has been ongoing since 2009. In the last few years, particulate emissions from the metallurgical complex have declined significantly. This work aims to assess the impact of this decrease on the level of the environmental burden of the study area by using analysis of AD fluxes of selected elements (Fe, Al, Mn, Zn, Pb, Cu, Cr, Cd, As) and dust particles.

**Emission and wind conditions in the area**

The study area is located in the Košice Basin, in the valley of the Hornád River in the eastern part of Slovakia. The industrial complex of iron and steel works is located about 10 km south to the southwest of the city center, with about 240,000 inhabitants. The second most significant source of emissions, the limekiln Carmeuse Slovakia, Ltd., and several other companies linked to metallurgical production with relatively marginal emissions operate directly on the ironworks site. Directly in the southern part of

the town, there is a heating plant (TEKO), which produces heat and electricity based on coal and natural gas. The annual registered PM emissions from these decisive sources in the studied area of Košice for the entire monitored period from 2009 to 2022 are shown in Tab. 1 [7]. In recent years, there has been a significant, several-fold decrease in PM emissions due to technological measures implemented in 2019. In addition to the registered emissions, the entire iron and steel works area is also an area source (about 10 km2) of fugitive PM emissions from handling raw materials and wastes, landfills, and other activities.

The surrounding mountains' configuration determines the study area's wind and climate conditions. The average annual precipitation is 625 mm, and the average annual temperature is 8.5 °C. The north-south orientation of the Košice basin is the most crucial factor for the formation of wind flow directions, which is documented by the wind rose in Fig. 1 and the data on the frequency of wind directions and wind speed processed in Tab. 2 from the station Košice – airport [8]. The prevailing wind directions are northerly (53.5%), and southerly (31.6%), and the occurrence of calms is 9.5%. In the southern, much wider part of the basin, there is a double calm (22%), also the prevailing flow direction changes to the northeast-southwest, shown in Tab. 3 from the station Veľká Ida [8].

Tab. 1. The annual registered PM emissions from decisive sources in the area of Košice [t].

| Source/Year | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 | 2018 | 2019 | 2020 | 2021 | 2022 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **TEKO[a]** | 56 | 92 | 90 | 96 | 76 | 85 | 37 | 2 | 2 | 2 | 4 | 8 | 5 | 6 |
| **Limekiln[b]** | 518 | 333 | 169 | 137 | 12 | 12 | 15 | 9 | 8 | 11 | 7 | 4 | 6 | 5 |
| **Other sources[c]** | 19 | 32 | 24 | 21 | 18 | 19 | 13 | 14 | 14 | 13 | 9 | 8 | 9 | 8 |
| **U.S. Steel K.** | 2368 | 2746 | 2923 | 3130 | 3302 | 3335 | 2882 | 2703 | 2668 | 2361 | 1102 | 275 | 461 | 401 |
| **Σ Emmisions[d]** | 2905 | 3111 | 3116 | 3288 | 3332 | 3366 | 2910 | 2726 | 2690 | 2385 | 1118 | 287 | 476 | 414 |

[a] - Municipal heating plant, [b] - Carmeuse Slovakia Ltd., [c] - Emissions from other companies on the site of iron and steel works, [d] – The sum of emissions from the area of the U. S. Steel Košice iron and steel works complex.

Tab. 2. The average frequency and wind speed from the station Košice – airport.

| Wind direction | N | NE | E | SE | S | SW | W | NW | CALM |
|---|---|---|---|---|---|---|---|---|---|
| **Average wind frequency [%]** | 36.3 | 5.1 | 2.2 | 3.6 | 15.6 | 13.0 | 2.6 | 12.1 | 9.5 |
| **Average wind speed [m.s$^{-1}$]** | 5.6 | 3.6 | 2.2 | 2.5 | 3.5 | 5.6 | 2.3 | 3.6 | 0 |

Tab. 3. The average frequency and wind speed from the station Veľká Ida.

| Wind direction | N | NE | E | SE | S | SW | W | NW | CALM |
|---|---|---|---|---|---|---|---|---|---|
| **Average wind frequency [%]** | 15.3 | 18.3 | 4.6 | 1.8 | 8 | 16.5 | 6.7 | 6.8 | 22 |
| **Average wind speed [m.s$^{-1}$]** | 5.7 | | 3.6 | | | | | | 0 |

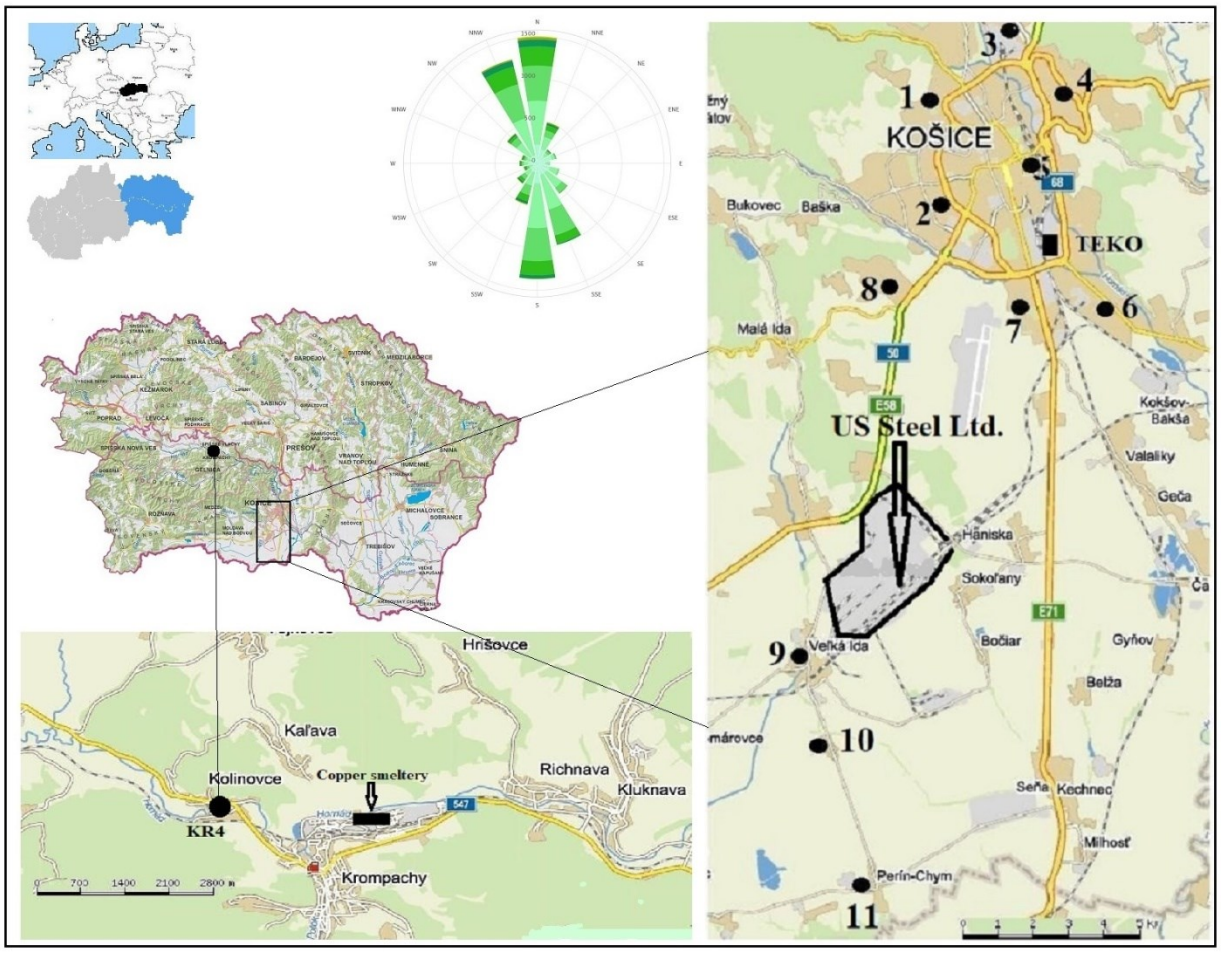


Fig. 1. Location of the AD sampling sites in the area of Košice (1-11) and the control site (KR4) and the wind rose for the Košice - airport station

**Material and methods**

AD samples were taken from eleven stations in urban, suburban, and rural environments in the Košice area, at a distance of 3 to 16 km from the primary emission sources of ironworks. Since 2009 in the case of stations KE1 to KE8, respectively since 2011 in the case of stations KE9 to KE11. Currently, sampling is taking place at six stations (KE1, KE2, KE7, KE9, KE11) and one control station (KR4) with a negligible impact of emissions from the subject area. The location of the sites is shown in Fig. 1. Additional relevant information about individual sites is processed in Tab. 4.

The methodology of sample collection, processing, analysis, and the technique used have been described in detail [9,10]. Total AD (wet and dry) was collected in open polyethylene containers mounted on four racks with a total sedimentation area of 490 cm2 with monthly collections (35 ± 5 days). The racks are placed on the roofs of residential dwellings, public buildings (urban and suburban environments), and farm buildings (rural environments) above the surrounding buildings' height, thus minimizing particle resuspension's impact. In the laboratory, the contents of the containers were transferred entirely to the filtration unit using ultrasonication and ultrapure deionized water. Subsequently, the analyte was separated into "soluble" and "insoluble" fractions (PM) - by vacuum filtration through a cellulose nitrate membrane filter (pore diameter 0.45 µm). The acidified soluble fraction was analyzed for the content of monitored elements directly after each collection. The insoluble, solid fraction (PM) of AD from monthly sampling was accumulated into a semi-annual sample in terms of the heating season, analyzed after its mineralization using the MWS - 3 Berghof microwave device as "summer" and "winter" periods (mid-April - mid-October). Total deposition data were obtained by adding both parts of the deposition. The elements were analyzed by atomic absorption spectroscopy (AAS) and inductively coupled plasma with mass spectrometry (ICP-MS) method using VARIAN AA240 FS with GTA 120 and Agilent 7700 devices. Ultrapure chemicals and water were used in the sample preparation and analysis procedures. For validation of the analytical results, standard reference materials NIEST No. 28 (Urban aerosols) and CTA-FFA-1 (Fine Fly Ash) and a blank sample prepared using the same reagents were used to control each set of analyses. Average daily fluxes of the parameters of interest were calculated based on the chemical analyses performed, gravimetric and volumetric evaluation of AD. The tools of the Data analysis package of Excel were used to calculate the correlation coefficients of the studied parameters and to evaluate their statistical significance.

**Results and discussion**

In Tab. 4, the weighted averages of the daily fluxes of particulate matter (insoluble fraction of AD) and the monitored elements from total AD are processed for all sampling sites and the monitoring period until October 2022. Significant differences in deposition were found for the individual sites, mainly depending on the distance from the ironworks and the specifics of their location. The deposition values of the monitored elements and PM from the sites in the urban development are relatively balanced.

The absolute highest values for all monitored parameters were measured at sampling point KE9, located closest to the ironworks, at a distance of 3 km in a southerly direction. The deposition level from this station exceeds by several times the AD fluxes of all monitored elements and PM recorded at urban stations. Compared to the control station KR4, the AD from sampling point KE9 was ca. 40, 29, 8, and 5 times higher for manganese, iron, chromium, aluminum, and PM, respectively. The differences between AD for the other monitored elements (Zn, Pb, Cu, Cd, As) are less pronounced. This is due to the location of the KR4 site within 2 km from the copper smelters in Krompachy, which are a significant source of emissions of these elements.

Tab. 4. The average daily fluxes of bulk atmospheric deposition of elements and PM ("PM - insoluble fraction") in the Košice area [μg.m$^{-2}$.day$^{-1}$].

| Site | Area[a] | D[km][c] | $N_{W/S}$[b] | PM | Fe | Al | Mn | Zn | Pb | Cu | Cr | Cd | As |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **KE1** | U | 14.0 | 14/13 | 36621 | 2722 | 1294 | 58 | 72 | 19.4 | 10.4 | 4.9 | 0.27 | 1.15 |
| **KE2** | U | 11.2 | 14/13 | 37526 | 2778 | 1359 | 56 | 61 | 20.6 | 9.4 | 5.2 | 0.21 | 1.17 |
| **KE3** | U | 16.7 | 7/8 | 43916 | 2933 | 1039 | 60 | 87 | 19.9 | 8.7 | 5.4 | 0.4 | 0.87 |
| **KE4** | U | 15.6 | 6/6 | 38840 | 3432 | 1007 | 64 | 83 | 9.8 | 9.3 | 4.8 | 0.27 | 1.14 |
| **KE5** | U | 12.9 | 6/6 | 83909 | 5214 | 1751 | 96 | 112 | 14.4 | 17.3 | 8.6 | 0.34 | 1.26 |
| **KE6** | U | 10.9 | 6/6 | 30919 | 2797 | 870 | 53 | 67 | 7.6 | 8.5 | 4.8 | 0.22 | 0.51 |
| **KE7** | SU | 8.9 | 14/13 | 44544 | 4775 | 1438 | 87 | 91 | 32.6 | 10.5 | 5.5 | 0.27 | 1.37 |
| **KE8** | SU | 8.6 | 8/8 | 31201 | 3265 | 1031 | 75 | 116 | 23.9 | 9.0 | 5.2 | 0.28 | 0.74 |
| **KE9** | I/R | 3.0 | 11/11 | 145778 | 23149 | 4608 | 923 | 180 | 79.5 | 31.9 | 28.3 | 0.59 | 3.59 |
| **KE10** | I/R | 5.1 | 11/11 | 123749 | 17826 | 3773 | 544 | 173 | 77.4 | 16.6 | 16.4 | 0.54 | 3.18 |
| **KE11** | R | 8.9 | 11/11 | 47498 | 3650 | 1538 | 68 | 78 | 21.5 | 11.3 | 4.3 | 0.18 | 1.37 |
| **KR4** | I/R | 43.2 | 13/12 | 30384 | 793 | 981 | 23 | 198 | 48.0 | 85.2 | 3.5 | 1.19 | 1.97 |

[a] - U – Urban, SU – Suburban, I – Industrial, R – Rural area; [c] – Number of analyzed winter/summer periods;
[b] – Distance from the sampling point to the center of the iron and steel works U.S. Steel Košice Ltd.,

The AD fluxes from the Košice area were compared with the AD levels of elements from different areas [10]. The measured levels at sites around ironworks were higher, mainly for iron, manganese, chromium, and aluminum, compared to urban environments. The most significant differences were found for iron deposition. The AD values from sampling site KE9 were approximately 15, 13, and 7 times higher than the measured values from the urban environment of Belgrade for iron, manganese, and chromium, respectively [11]. On the other hand, the fluxes of iron, aluminum, and manganese in this study were comparable to those reported for the Aliaga region with the metallurgical industry in Turkey [12]. The average iron deposition at urban sites from Košice and rural areas was 2 to 3 and 5 to 7 times higher, respectively, compared to values from urban and rural areas. The AD of the other monitored elements was comparable to the measured values in urban environments [10].

Pearson's correlation analysis assessed the statistical dependence between the atmospheric deposition of individual elements and PM. Pearson's correlation coefficients are summarized in Tab. 5. Very high to high (r = 0.920 to 0.801) statistically significant correlation coefficient values (p-value 0.01) were found between manganese, iron, and chromium. High values of correlation coefficients (r = 0.800 to 0.701) have these elements with a dominant origin in the emissions of ironworks with solid particles and aluminum. Medium to low correlation values (r = 0.565 to 0.369) were detected in descending order with zinc, lead, arsenic, cadmium, and copper.

Tab. 5. Pearson's correlation coefficients between the atmospheric deposition of the observed parameters (n = 214, p-value 0.01).

| | PM | Fe | Al | Mn | Zn | Pb | Cu | Cr | Cd | As |
|---|---|---|---|---|---|---|---|---|---|---|
| **PM** | 1 | | | | | | | | | |
| **Fe** | 0.814 | 1 | | | | | | | | |
| **Al** | 0.777 | 0.680 | 1 | | | | | | | |
| **Mn** | 0.800 | 0.920 | 0.701 | 1 | | | | | | |
| **Zn** | 0.565 | 0.520 | 0.355 | 0.532 | 1 | | | | | |
| **Pb** | 0.413 | 0.670 | 0.307 | 0.513 | 0.357 | 1 | | | | |
| **Cu** | 0.316 | 0.369 | 0.248 | 0.457 | 0.311 | 0.181 | 1 | | | |
| **Cr** | 0.732 | 0.801 | 0.613 | 0.910 | 0.513 | 0.384 | 0.529 | 1 | | |
| **Cd** | 0.458 | 0.464 | 0.347 | 0.509 | 0.562 | 0.443 | 0.146 [a] | 0.465 | 1 | |
| **As** | 0.591 | 0.531 | 0.590 | 0.455 | 0.296 | 0.465 | 0.212 | 0.386 | 0.323 | 1 |

[a] – p-value 0.05

The values of atmospheric deposition of the monitored parameters for individual sampling points show variability between summer and winter periods but also within the season itself, which is documented by the processed data in Tab. 6 and Fig. 2.

In Tab. 6, the ratio (RS/W) between the average AD of PM and the investigated elements in summer and winter from the six active sites for the whole monitoring period is processed. The deposition of PM, aluminum, and, at several sampling sites, also for arsenic, is about twice as high in the summer period. In the case of PM and aluminum, this is due to better climatic conditions for wind erosion and resuspension of particles from the soil horizon, road traffic, and agricultural and construction activities in the summer.

For the other monitored elements, relatively balanced AD values were found for both periods, with ratios ranging from 0.89 to

1.20 (median). Minor seasonal differences were found for sampling point KE9 which is the most affected by emissions from the ironworks.

Tab. 6. The ratio between summer and winter atmospheric deposition of the PM and elements

| Site | PM | Fe | Al | Mn | Zn | Pb | Cu | Cr | Cd | As |
|---|---|---|---|---|---|---|---|---|---|---|
| **KE1** | 1.84 | 0.78 | 1.87 | 0.85 | 1.17 | 0.87 | 0.89 | 1.11 | 0.86 | 1.09 |
| **KE2** | 1.88 | 0.76 | 2.11 | 0.80 | 1.13 | 0.73 | 1.17 | 1.03 | 0.69 | 1.86 |
| **KE7** | 1.54 | 0.51 | 1.87 | 0.61 | 1.72 | 0.53 | 1.13 | 0.89 | 1.22 | 1.56 |
| **KE9** | 1.60 | 1.07 | 1.42 | 1.12 | 0.97 | 0.92 | 0.33 | 1.00 | 1.18 | 1.14 |
| **KE10** | 2.01 | 1.12 | 2.18 | 1.26 | 1.69 | 1.08 | 1.50 | 0.99 | 2.20 | 1.96 |
| **KE11** | 2.63 | 1.20 | 2.72 | 1.64 | 1.02 | 1.32 | 1.59 | 1.00 | 1.58 | 2.44 |
| **Median** | **1.86** | **0.93** | **1.99** | **0.99** | **1.15** | **0.89** | **1.15** | **1.00** | **1.20** | **1.71** |

For iron and manganese, exciting differences between summer and winter were found at sampling points located north of the ironworks KE1, KE2, and KE7, with RS/W ratios ranging from 0.51 to 0.85. Conversely, higher deposition in the summer period was found at the south-located sampling points KE9, KE10, and KE11, with RS/W ratios ranging from 1.07 to 1.62. Iron and manganese originate to a decisive extent from ironworks emissions but are also typical elements of the Earth's crust. For this reason, their higher AD fluxes in winter are somewhat surprising. The specific wind conditions in the Košice basin can explain this fact. In the winter half of the year, in wind speed classes up to 5 m.s-1, southerly flow prevails; also, at higher altitudes above the terrain at low wind speeds, the representation of the southerly direction is higher than at the bottom of the basin. In the frequency of higher wind speeds, the winds of northerly directions prevail significantly. This condition in winter provides better conditions for the sedimentation of particles at sites located north of the main emission source, despite the dominant northerly flow in the area.

The development of the total atmospheric deposition of dust particles, iron, manganese, zinc, chromium, cadmium, and the sum of annual PM emissions from the ironworks complex for three sampling points, namely KE1, KE2, and KE9, separately for the summer and winter periods is shown in Fig. 2. Pearson correlation coefficients between PM emissions from the ironworks complex and atmospheric deposition of PM and all monitored elements separately for the whole, summer, and winter seasons are elaborated in Tab. 7. Since the winter AD sampling periods (October-April) do not coincide with the calendar year, the averages of annual emissions from two consecutive years were used for the winter period for the graphical representation and calculations. As can be seen from the graphical comparison, the order of magnitude decrease in emissions is not reflected by an adequate decrease in deposition, even for elements relatively closely associated with ironworks emissions, such as iron, manganese, and chromium. However, a significant decrease was observed for most elements, more pronounced in the winter period, corresponding with the values of the correlation coefficients treated in Tab. 7.

Relatively higher positive correlation coefficient values were found between emissions and atmospheric deposition of the observed parameters for the whole period and all sampling points, in decreasing order for iron ( r = 0.283 - 0.818), zinc (0.305 - 0.742), manganese (0.253 - 0.683) and chromium (0.317 - 0.600). Relatively lower positive values were found for cadmium (0.127 -0.534), lead (0.165 - 0.457), copper (0.169 - 0.356), and PM (0.045 - 0.456). The minimum level of dependence with mostly negative and low values of correlation coefficients was found between emissions and AD of aluminum and partially arsenic. The highest absolute correlation values for most parameters for the whole period and individual seasonal periods were found for sampling point KE9, located

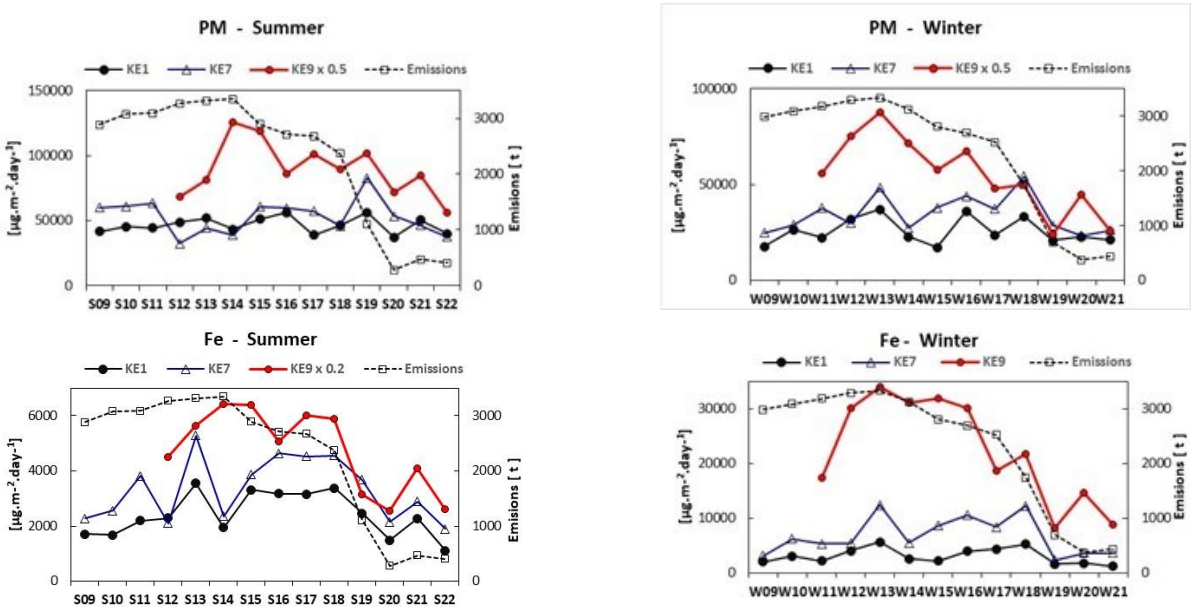


Fig. 2**.** Development of atmospheric deposition of PM, iron, manganese, zinc, chromium, cadmium, and the sum of annual emissions of particulate pollutants from the area of the U. S. Steel Košice iron and steel works complex from 3 sites in summer and winter ( S09 – summer 2009, W09 – winter 2009 – 2010, etc.)

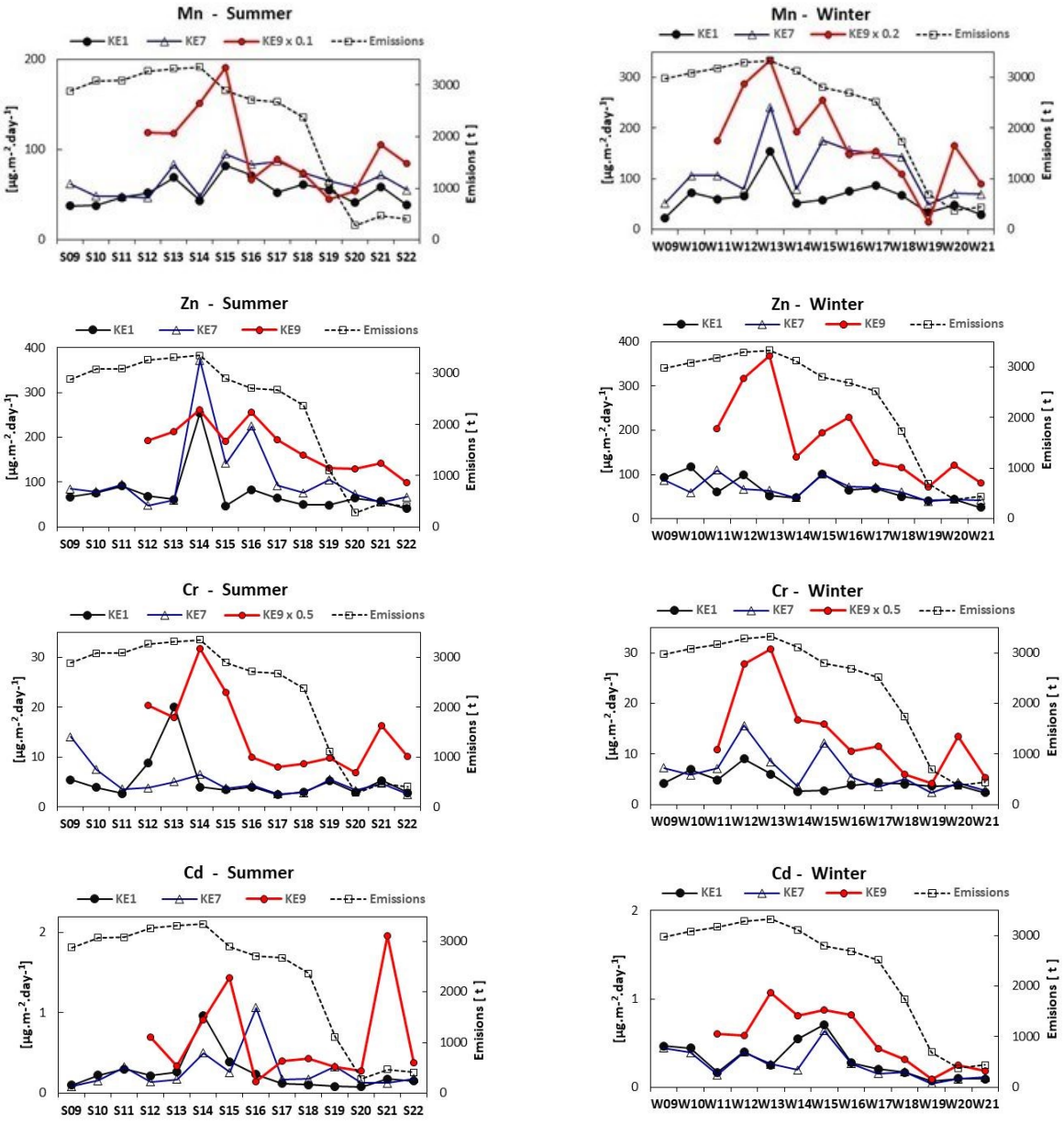


Fig. 2. Continued from Fig. 2.

closest to the ironworks site. When comparing the summer and winter periods, generally higher values of the calculated correlation coefficients for most of the monitored parameters were observed in the winter half of the year. This increase was most pronounced in the case of dust particles, which corresponds with the results of the analysis of the annual PM run elaborated in Tab. 6. In the winter half of the year, PM emissions from other emission sources are significantly lower, and the contribution of emissions from metallurgical production is more dominant than in summer.

During 2019, due to the installation of new dedusting equipment in the ironworks, there was a big drop in the recorded dust particulate emissions, as shown in Tab. 1 and Fig. 2. Fig. 3 presents this decrease's impact on the average AD fluxes of monitored elements and PM at individual sites in the Košice area and control site KR4.

The "Before" period is the weighted average AD of individual elements and PM from seven winter and seven summer half-years from winter 2011-2012 to summer 2018. The "After" period is the AD of 3 winters and three summer half-years from winter 2019 - 2020 to summer 2022.

Tab. 7. Pearson correlation coefficients between PM emissions from the iron and steel works complex and atmospheric deposition of monitored parameters for individual sampling sites. (a) - for the whole period, b) - summer half-years, c) - winter half-years; in **bold** p-value 0.05, * - p-value 0.01)

| Site | n | PM | Fe | Al | Mn | Zn | Pb | Cu | Cr | Cd | As |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **a)** | | | | | | | | | | | |
| **KE1** | 27 | 0.089 | **0.412** | -0.380 | 0.349 | **0.442** | 0.214 | 0.373 | 0.317 | **0.534*** | -0.133 |
| **KE2** | 27 | 0.093 | **0.443** | -0.207 | **0.423** | **0.428** | 0.197 | 0.211 | **0.447** | **0.462** | 0.090 |
| **KE7** | 27 | 0.045 | 0.283 | -0.247 | 0.253 | 0.305 | 0.165 | 0.160 | **0.422** | 0.348 | 0.028 |
| **KE9** | 22 | **0.456** | **0.818*** | -0.157 | **0.627*** | **0.742*** | **0.457** | 0.356 | **0.600*** | 0.228 | -0.076 |
| **KE10** | 22 | 0.111 | **0.672*** | **-0.424** | **0.683*** | 0.365 | 0.343 | 0.351 | 0.393 | 0.228 | **-0.509** |
| **KE11** | 22 | 0.100 | **0.758*** | -0.192 | **0.461** | **0.656*** | 0.340 | 0.169 | 0.383 | 0.127 | 0.170 |
| **b)** | | | | | | | | | | | |
| **KE1** | 14 | 0.160 | 0.427 | -0.531 | 0,078 | 0.383 | 0.212 | 0.280 | 0.296 | 0.445 | -0.336 |
| **KE2** | 14 | 0.062 | 0.492 | -0.338 | 0,205 | 0.451 | 0.211 | 0.266 | 0.287 | 0.418 | 0.138 |
| **KE7** | 14 | -0.056 | 0.336 | -0.315 | -0,062 | 0.327 | 0.148 | -0.004 | 0.276 | 0.208 | 0.048 |
| **KE9** | 11 | 0.472 | **0.850*** | **-0.639** | **0,567** | **0.845*** | 0.457 | **0.568** | **0.554** | -0.078 | -0.448 |
| **KE10** | 11 | 0.177 | **0.820*** | **0.775*** | **0,770*** | 0.451 | 0.380 | 0.440 | 0.220 | 0.254 | -0.720 |
| **KE11** | 11 | 0.139 | **0.818*** | -0.443 | **0,649** | 0.651 | 0.331 | 0.177 | 0.145 | -0.002 | 0.296 |
| **c)** | | | | | | | | | | | |
| **KE1** | 13 | 0.268 | 0.456 | -0.343 | 0.467 | **0.646** | 0.244 | 0.462 | 0.482 | 0.655 | 0.019 |
| **KE2** | 13 | 0.534 | 0.516 | -0.040 | 0.583 | 0.404 | 0.225 | 0.173 | 0.597 | 0.571 | 0.043 |
| **KE7** | 13 | 0.281 | 0.391 | -0.248 | 0.424 | **0.624** | 0.215 | 0.290 | 0.567 | 0.599 | -0.005 |
| **KE9** | 11 | **0.859*** | **0.827*** | 0.520 | **0.730** | **0.744*** | 0.483 | 0.433 | **0.656** | **0.848*** | 0.151 |
| **KE10** | 11 | 0.456 | 0.548 | -0.129 | **0.687** | 0.474 | 0.328 | 0.350 | **0.622** | 0.479 | -0.283 |
| **KE11** | 11 | **0.686** | **0.759*** | 0.436 | 0.524 | **0.672** | 0.356 | 0.202 | 0.564 | 0.387 | 0.014 |

Particulate matter emissions decreased on average by a factor of 7.5 during this period. However, a decrease in atmospheric deposition adequate to the change in emissions was found only for lead at individual sites in the 3 to 7.5 times the preceding AD level. The AD of the other elements decreased less significantly. In descending order, a decrease was recorded in iron, cadmium, copper, manganese, zinc, chromium, and PM. When averaged over all sites, the AD of iron and cadmium, copper, manganese, chromium, and zinc decreased by a factor of 2, 1.8, 1.6, and 1.3 times, respectively, for iron, copper, manganese, chromium, and zinc, and PM. The highest decrease was found at site KE9, closest to the ironworks. In the case of aluminum, there was even a slight increase, except at site KE9. For arsenic, only a slight decrease was recorded at sites located to the north and some increase at sites located south of the ironworks. At control site KR4, except for cadmium, no significant changes in AD fluxes were recorded during the assessment period.

These findings show that the decline in recorded emissions from the ironworks is significantly affecting the level of AD at the monitored sites. However, the decreased fluxes of the monitored AD parameters are not directly proportional to this decrease in emissions. AD naturally decreases with distance from the emission source, which is related to the fact that the dedusting equipment significantly eliminates the coarser fraction of emitted particles, subject to more rapid sedimentation. For the AD of trace elements, the variability in origin and hence the qualitative composition of the feedstock for the production process is also likely to impact the AD level. Although ironworks emissions are the dominant source for most of the parameters of interest in the study area, they are not the only source. Local orographic, climatic, and wind conditions and other specifics of the location of individual sites also affect AD.

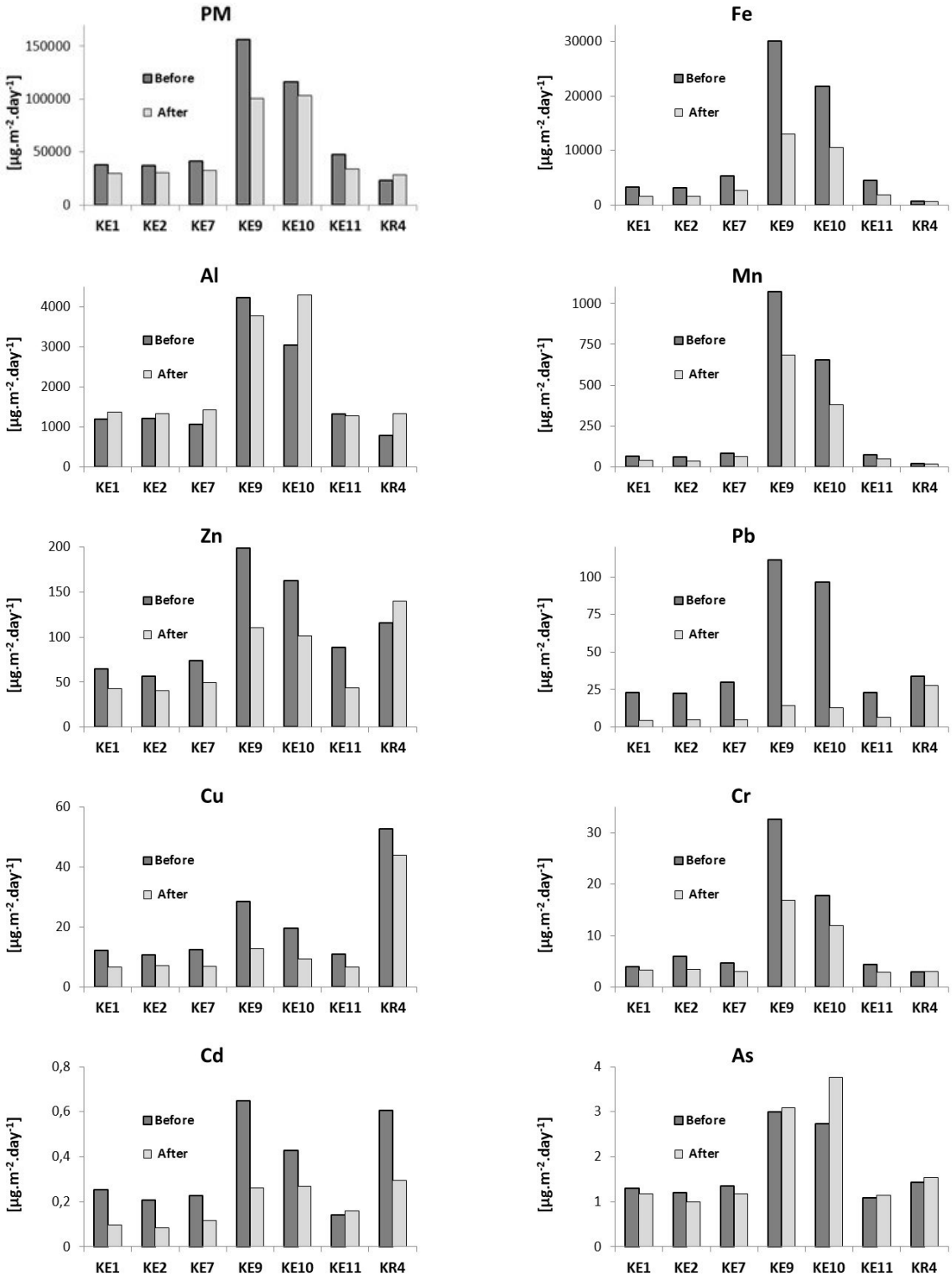


Fig. 3. Comparison of average AD fluxes of observed parameters at sites in the Košice area and the control site "before" and "after" the massive decrease in emissions from the metallurgical complex in 2019.

**Conclusion**

Detailed analysis of AD dust particles and selected elements as markers of specific emission sources provide essential information for assessing the level of immission burden and potential environmental risks in the study area.

- Emissions associated with the metallurgical industry have a decisive impact mainly on the AD of manganese, iron, chromium, particulate matter, zinc, and aluminum, but also, to a lesser extent, on the AD of the other monitored elements.
- Correlation analysis confirmed a statistically significant dependence between the amount of emissions and the mass fluxes of AD for iron, zinc, manganese, and chromium for most of the sampling sites.

- The potential of immission load of the urban environment of Košice by emissions from the metallurgical industry is significantly higher in the winter due to local specific meteorological conditions.
- The more than sevenfold decrease in emissions significantly affected the AD of most of the monitored parameters, but their decrease was not so significant except for the AD of lead. The average AD of the elements strongly associated with ironworks emission sources, namely iron, manganese, chromium, and zinc, decreased approximately twofold.
- The amount of emissions is only one of several factors that affect the quantity of fluxes of the monitored AD parameters. In addition to seasonal factors, local meteorological, climatic, orographic, and other local conditions and specifics also play an important role.

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