Characteristics and Seasonal Variations of Atmospheric Deposition of Selected Elements in the Urban and Industrial Environment of Košice (Slovakia)

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Abstract. This study aims to evaluate the impact of local emission sources on the environmental load through a detailed analysis of the atmospheric deposition (AD). The main sources of pollution are neighboiring iron and steelworks and typical urban sources, such as the heating plant, transport, construction, etc. Total atmospheric deposition, i.e. both wet and dry ones, were sampled from eleven sampling sites that have been placed on the roofs above the height of the surrounding buildings at a distance of 1 to 16 kilometers from the main source of pollution in the urban, suburban and rural areas. The atmospheric deposition fluxes of selected elements (Fe, Al, Mn, Zn, Pb, Cu, Cr, Cd, As) were determined separately for “water-soluble” and “insoluble phase” (particulate matter - PM) as well as in terms of the heating season for summer and winter half-year. The results from 2009–2020 are introduced. The average Fe deposition at urban stations in Košice was 2-3 times higher, compared with other urban areas. The very high values of iron deposition (9,181) and manganese (348 mg.m⁻².yr⁻¹) were measured mainly at sites near the ironworks. The highest values of correlation coefficients were calculated by Pearson correlation analysis for the elements Fe, Mn and Cr but also for Al and PM. Higher values of correlation coefficients were calculated for the winter period. The monitored elements are bound to the insoluble component AD in the order of Fe, Al, Cr, Pb, Mn and As. Cadmium and zinc are preferably bound to the soluble phase for sites north of the ironworks. Significant differences for fluxes of AD of the most observed parameters were found between the summer and winter periods. In winter, higher values of AD were found for the elements Fe, Pb, Mn, Cr, and Cd. In the case of zinc and arsenic higher values were recorded in the summer period. The share of emission sources of iron and steelworks on the fluxes of iron at the urban sites in winter was more than doubled compared to the summer period. The smallest seasonal differences for all observed components were found at localities near the ironworks. Detailed analysis of AD showed that in addition to Fe, Mn, and Cr, the ironworks complex is also a source of dust particles, aluminum and other observed elements in descending order of lead, zinc, copper, arsenic and cadmium.

1. Introduction
Air pollution by particulate matter (PM) can present a serious problem from an environmental and health risk to humans [1,2]. Emissions of these particles, mainly from large anthropogenic sources are relatively known, quantified and inventoried [3,4]. However, in a real immission environment, it is difficult to determine the origin and source of these particles, because they originate from a mixture of various local anthropogenic and natural resources and long-range transport. There are also present

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secondary particles from photochemical reactions. The knowledge of their chemical composition and other characteristics is necessary to identify their sources, to understand transport processes and also to be able to define measures to eliminate possible environmental and health risks. Metals bound to particulate matter are considered very good markers of specific anthropogenic and natural sources of pollution [5]. Particulate matter from the atmosphere reaches the earth’s surface by atmospheric deposition (AD) processes. The study of AD of selected metals and trace elements and their interrelationships can be a suitable tool for identifying the origin and sources of particulate matter as well as a certain indicator of environmental quality. For this reason, studies dealing with AD in terms of various parameters and aspects are available [6-22].

In addition to typical urban sources of pollution, the Košice region has also been burdened for a long time by the iron and steelworks - the largest industrial source of pollution in Slovakia. The paper presents some results of a study of total AD focused on deposition fluxes of selected elements (Fe, Al, Mn, Zn, Pb, Cu, Cr, Cd and As) and PM in relation to local emissions from 2009 to 2020. This study aims to evaluate the impact of local emission sources on the environmental load through a detailed analysis of the atmospheric deposition.

2. Description of the study area
The studied region is located in the Košice Basin, in the river valley Hornád with north-south orientation in the eastern part of Slovakia. Košice has a population of 234 000. The wind conditions are determined by the orography of the valley. There is the evident prevalence of north (53.5%) and south (31.6%) winds, the occurrence of calm is 9.5%. The average annual amount of precipitation is 625 mm, mean annual temperature is 8.5 °C. 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 of 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 the complex. Directly, in the southern part of the city, a heating plant (TEKO) is located that produces heat and electricity from coal and natural gas. The emissions produced by iron and steel resources such as ores, coke plants, blast furnaces, energetics, steelworks are qualitatively different. Inventory emissions of PM and selected metals from crucial sources of pollution in the area are processed in Table 1 and Table 2 [4]. In addition to the registered emissions, the entire area of iron and steelworks is also an area source (more than 10 km²) of fugitive emissions of dust particles from the handling of raw materials and waste, waste dump and other activities.

3. Materials and methods
Bulk atmospheric deposition (wet + dry) has been collected monthly (35 ± 5 days) from eleven sites in the urban, suburban and rural area in the vicinity of iron and steel industry complex since June 2009 (sites No. 1-8) and October 2011 (sites No. 9-11) to October 2020. In the case of sites No. 4, 5, 6 and sites No. 3 and 8 samplings was completed in April 2014 and April 2017, respectively. Map of the study area and sampling stations are illustrated in Figure 1 and further information about the sites is listed in Table 3. The four open cylindrical polyethylene containers with a total surface area of 490 cm² fitted on a stand were used for sampling [16-20]. In the city, the stands (sampling 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 and surrounding buildings, 4 - 12 m in the case of suburban and rural sites with low buildings (No. 7 – 11) respectively. In the laboratory, the contents of the sampling vessels were washed and completely transferred to the filtration unit using ultrasound and ultrapure deionized water. After vacuum filtration through membrane cellulose nitrate filter (0.45 µm), into the “water-soluble and “insoluble fraction” (PM). The soluble fraction after filtration and stabilization of samples with addition HNO₃ was directly prepared for chemical analysis.
Table 1. The annual emissions of PM from the largest sources in the Košice area [t.year⁻¹].

| Source/Year | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 | 2018 | 2019 |
|-------------|------|------|------|------|------|------|------|------|------|------|------|
| TEKO⁴       | 56   | 92   | 90   | 96   | 76   | 85   | 37   | 2    | 2    | 2    | 4    |
| Limekiln⁵   | 518  | 333  | 169  | 137  | 12   | 12   | 15   | 9    | 8    | 11   | 7    |
| U.S. Steel. Ltd. | 2368 | 2746 | 2923 | 3130 | 3302 | 3335 | 2882 | 2703 | 2664 | 2319 | 1075 |

⁴ – City heating plant, ⁵ – Carmeuse Slovakia Ltd.

Table 2. The annual emissions of selected metals from U.S. Steel Košice. Ltd. [t.year⁻¹].

| Element | 2009  | 2010  | 2011  | 2012  | 2013  | 2014  | 2015  | 2016  | 2017  | 2018  | 2019  |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Mn      | 2.42  | 2.39  | 2.26  | 2.81  | 3.09  | 3.96  | 7.69  | 0.73  | 0.91  | 0.67  | 0.51  |
| Zn      | 7.14  | 8.55  | 8.04  | 5.13  | 2.99  | 2.80  | 3.19  | 6.40  | 7.04  | 6.53  | 2.20  |
| Pb      | 13.4  | 16.3  | 17.8  | 17.8  | 17.2  | 21.3  | 20.9  | 60.7  | 61.2  | 59.3  | 21.9  |
| Cu      | 0.61  | 0.79  | 0.93  | 0.01  | 0.001 | 0.001 | 0.002 | 0.002 | 0.01  | 0.12  | 0.30  |
| Cr      | 0.71  | 0.79  | 0.88  | 0.19  | 0.04  | 0.05  | 0.05  | 0.03  | 0.05  | 0.06  | 0.12  |
| As      | 0.16  | 0.15  | 0.12  | 0.03  | 0.03  | 0.03  | 0.04  | 0.12  | 0.24  | 0.26  | 0.19  |
| Cd      | 0.11  | 0.13  | 0.15  | 0.06  | 0.06  | 0.07  | 0.07  | 0.13  | 0.12  | 0.13  | 0.04  |

Figure 1. Location of the sampling sites
The insoluble fraction for analysis was prepared by cumulation of monthly samples into the one semi-annual sample – summer and winter period (mid-April – mid-October) after its mineralization by acid microwave decomposition (MWS - 3 Berghof). The volume of the water-soluble fraction was determined by a graduated vessel, the differential gravimetry of the filters was determined by microbalances with a readability of 0.01 mg. The elements were analyzed by the atomic absorption spectroscopy method using the device VARIAN AA240 FS with GTA 120 until October 2012, after that time the elements were determined by inductively coupled plasma with mass spectrometry method (ICP-MS) on the device Agilent 7700. Ultrapure reagents were used in procedures sample preparation and analysis and checked using standard reference materials NIEST No. 28, Urban Aerosols and CTA-FFA-1, Fine Fly Ash. One blank sample was prepared using the same reagents and amounts to check of each set of analyzes.

Table 3. The average daily fluxes of bulk atmospheric deposition of elements and PM (“insoluble fraction”) in the Košice area [µg.m⁻².day⁻¹].

| Site | Areaa | Nw/b | D [km]c | PM  | Fe  | Al  | Mn  | Zn  | Pb  | Cu  | Cr  | As  | Cd  |
|------|-------|------|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1    | U     | 12/12| 13.4    | 37127| 2930| 1227| 63  | 92  | 22  | 11.6| 5.3 | 1.21| 0.30|
| 2    | U     | 12/12| 10.7    | 38407| 2994| 1329| 60  | 72  | 24  | 10.8| 5.7 | 1.29| 0.24|
| 3    | U     | 7/8  | 16.3    | 43916| 2933| 1039| 60  | 87  | 20  | 8.7 | 5.4 | 0.87| 0.40|
| 4    | U     | 6/6  | 15.1    | 38840| 3432| 1007| 64  | 83  | 10  | 9.3 | 4.8 | 1.14| 0.27|
| 5    | U     | 6/6  | 12.2    | 83909| 5214| 1751| 96  | 112 | 14  | 17.3| 8.6 | 1.26| 0.34|
| 6    | U     | 6/6  | 10.4    | 30919| 2797| 870 | 53  | 67  | 8   | 8.5 | 4.8 | 0.51| 0.22|
| 7    | SU    | 12/12| 8.6    | 46638| 5115| 1401| 94  | 110 | 38  | 13.3| 5.9 | 1.49| 0.32|
| 8    | SU    | 8/8  | 8.5    | 31201| 3265| 1031| 75  | 116 | 24  | 9.0 | 5.2 | 0.74| 0.28|
| 9    | I/R   | 9/9  | 3.6    | 154786| 25153| 4280| 953 | 203 | 95  | 37.0| 29.7| 3.70| 0.58|
| 10   | I/R   | 9/9  | 5.5    | 126865| 19508| 3335| 575 | 203 | 92  | 19.7| 17.4| 2.95| 0.61|
| 11   | R     | 9/9  | 9.0    | 47565| 4001| 1420| 72  | 94  | 26  | 13.7| 4.5 | 1.50| 0.19|

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

4. Results and discussion

The time-weighted average daily fluxes (µg.m⁻².day⁻¹) of observed elements and particulate matter - PM (“water-insoluble” part of AD) from total bulk deposition for all sampling sites and the whole monitored period from June 2009 to October 2020 are reported in Table 3. Elemental and PM deposition fluxes at different sites in the study area revealed significant differences in terms of spatial and time variations, depending mainly on the locations of the sites, distances to emission sources, different activities and meteorological parameters. The values of deposition of observed elements and PM from urban sites are relatively balanced, without increased values at site 5. Deposition fluxes at the site were significantly affected mainly by the nearby heating plant (TEKO) and the construction of a shopping center during the monitored period. The lower and comparable values were measured in the case of urban and suburban sites 6 and 8 respectively, which are located relatively closer to iron and steelworks but are located on the edges of the main direction of the flow of the wind and the smoke cloud. On the contrary, the level of deposition of all monitored parameters was significantly higher at the suburban site 7, which is located at approximately the same distance but in the middle of the trajectory of the smoke cloud. The highest values were measured in industrial/rural localities 9 and 10 located south of the ironworks in their immediate vicinity for all monitored parameters. The level of deposition from these two stations exceeded the deposition fluxes recorded at urban stations several
times. For example, the ratio between the average atmospheric deposition from sampling site 9 and the urban site 1 was in the range of 1.9 to 15.1 for the observed parameters (Cd = 1.9, As = 3.1, Cu = 3.2, Al = 3.5, Pb = 4.3, PM = 4.2, Cr 5.6, Fe = 8.1, Mn = 15.1). In the previous study, the dependence between elements and PM fluxes and the distance from the ironworks was studied using regression analysis. Significant dependence was found in descending order, for Mn, Fe, PM, Cr, Al and partly for Zn. In the case of lead and copper, only a minor dependence was found [19].

The annual deposition fluxes of the elements from the present study area were compared with results from different areas in Table 4. The results indicated that annual elemental deposition fluxes were higher mainly in the case Fe, Mn, Cr and Al, than the ones measured in the previous studies. The most significant differences were found for the deposition of iron. For example, at industrial site 9, deposition fluxes of Fe, Mn and Cr were 15.5, 13.3 and 6.8 times higher respectively, than in the urban area of Belgrade [10]. On the other hand, the fluxes of Fe, Al and Mn in the present study were comparable to those reported for industrial sites in iron - steel industrial region Aliaga, Turkey[8]. The average Fe deposition at urban stations in Košice was 2-3, respectively 5-7 times higher compared with urban respectively rural areas. The values of other observed elements were comparable with their average values measured in an urban environment.

Table 4. Annual elemental depositions fluxes in different regions [mg.m\(^{-2}\).yr\(^{-1}\)]

| Location                  | Study area\(^a\) | Fe  | Al  | Mn  | Zn  | Pb  | Cu  | Cr  | As  | Cd  | Ref. |
|---------------------------|------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|
| Košice No. 1              | U                | 1069| 448 | 23  | 34  | 8.0 | 4.2 | 1.9 | 0.44| 0.11| PS\(^b\) |
| Košice No. 7              | SU               | 1867| 511 | 34  | 40  | 13.9| 4.9 | 2.2 | 0.54| 0.12| PS   |
| Košice No. 9              | I/R              | 9181| 1562| 348 | 74  | 34.7| 13.5| 10.8| 1.35| 0.21| PS   |
| Aliaga, Turkey            | I/R              | 6020| 1173| 255 | 881 | 189 | 44.8| 23  | 2   | 0.13 | [8]   |
| Belgrade, Serbia          | U                | 594 | 26.2| 41.4| 21.7| 34.5| 1.6 | 0.22|     |      | [10] |
| Cartagena, Spain          | M/R              | 6.7 | 221 | 4.6 |     |     |     | 0.3 | 0.01|      | [20] |
| Cordoba, Argentina        | U/R              | 4161| 51.3| 108 | 6.5 | 10.9| 8.1 | 1.61| 0.13|      | [14] |
| Delta Pearl River, China  | U/SU             | 555 | 9   | 104 | 12.7| 18.6| 6.4 | 0.07|      | [22] |
| Northern France           | U/SU             |     | 15.6| 2.2 | 3.9 |     |     |     | 0.05|      | [6]   |
| Czech Republic            | R                | 291 | 178 | 13.6| 54.3| 8.8 | 2.9 | 0.7 | 0.47| 0.15 | [21] |
| England and Wales         | R                |     |     | 22.1| 5.4 | 5.7 | 0.8 | 0.31| 0.19|      | [11] |
| Massachusetts Bay         | R                | 140 | 102 | 3.4 | 7.8 | 1.8 | 2.5 | 2.7 | -   | 0.27 | [12] |

\(^a\) - U – Urban, SU – Suburban, I – Industrial, R – Rural; M – former mining district, \(^b\) – Present study

Table 5 reports the average percentage representation of the deposition of trace elements bound to the "water-insoluble"(PM) part of AD for each sampling point. The elements in order Fe, Al, Cr, Pb, Mn, As and partially Cu are predominantly bound to “water-insoluble” fraction of bulk atmospheric deposition (median). Cadmium and zinc are preferably bound to the soluble phase for sites north of the ironworks except for site 5 due to the impact of emissions from the heating plant. In the south, in the vicinity of ironworks, all monitored metals are preferentially bound mainly to the insoluble fraction of AD with a relatively higher representation. Except for monitored elements’ properties, it is probably related to average size and thus with the surface of the particles. With increasing distance from the source of particulate emissions, the proportion of smaller particles on their overall particle size distribution is rising.
Table 5. The average element abundances in insoluble fraction (PM) [%].

| Site | Fe   | Al   | Mn   | Zn   | Pb   | Cu   | Cr   | As   | Cd   |
|------|------|------|------|------|------|------|------|------|------|
| 1    | 98.7 | 98.1 | 74.1 | 43.2 | 84.1 | 45.7 | 83.6 | 62.8 | 43.1 |
| 2    | 98.0 | 97.9 | 77.0 | 41.8 | 83.0 | 48.1 | 87.6 | 66.2 | 42.4 |
| 3    | 99.2 | 98.8 | 80.4 | 40.7 | 82.2 | 50.1 | 84.1 | 68.6 | 44.2 |
| 4    | 99.3 | 97.3 | 72.5 | 40.6 | 79.8 | 50.8 | 91.7 | 68.5 | 48.1 |
| 5    | 99.4 | 99.0 | 88.6 | 86.8 | 86.7 | 55.9 | 87.9 | 79.7 | 59.2 |
| 6    | 99.4 | 97.9 | 72.3 | 45.5 | 85.8 | 51.2 | 88.6 | 77.9 | 45.1 |
| 7    | 99.2 | 97.8 | 79.4 | 50.7 | 81.5 | 50.5 | 86.8 | 75.2 | 44.5 |
| 8    | 99.1 | 97.7 | 75.4 | 50.1 | 83.4 | 47.5 | 87.3 | 72.1 | 38.7 |
| 9    | 99.7 | 95.9 | 94.4 | 83.6 | 92.3 | 72.3 | 96.3 | 86.1 | 75.0 |
| 10   | 99.6 | 97.5 | 92.4 | 81.3 | 93.0 | 60.7 | 94.0 | 84.6 | 73.0 |
| 11   | 98.3 | 97.9 | 85.0 | 62.1 | 81.3 | 42.4 | 85.3 | 77.8 | 53.5 |
| Median | 99.2 | 97.9 | 79.4 | 50.1 | 83.4 | 50.5 | 87.6 | 75.2 | 45.1 |

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

| Site | PM  | Fe   | Al   | Mn   | Zn   | Pb   | Cu   | Cr   | As   | Cd   |
|------|-----|------|------|------|------|------|------|------|------|------|
| 1    | 1.80| 0.76 | 1.84 | 0.88 | 1.55 | 0.84 | 0.94 | 1.12 | 1.08 | 0.86 |
| 2    | 1.82| 0.74 | 2.04 | 0.80 | 1.32 | 0.72 | 1.32 | 1.07 | 2.01 | 0.66 |
| 3    | 1.93| 0.82 | 1.48 | 0.85 | 1.48 | 1.12 | 0.99 | 0.84 | 1.72 | 1.30 |
| 4    | 1.76| 0.55 | 1.13 | 0.56 | 0.78 | 0.50 | 0.69 | 0.69 | 2.26 | 0.87 |
| 5    | 2.19| 0.79 | 1.62 | 0.91 | 1.72 | 0.74 | 0.95 | 0.90 | 1.73 | 0.87 |
| 6    | 1.65| 0.70 | 1.39 | 0.74 | 0.79 | 0.48 | 1.04 | 0.56 | 1.00 | 0.54 |
| 7    | 1.51| 0.50 | 1.84 | 0.62 | 2.08 | 0.52 | 1.55 | 0.89 | 1.68 | 1.35 |
| 8    | 1.67| 0.70 | 1.74 | 0.70 | 1.38 | 0.70 | 0.89 | 0.70 | 1.13 | 0.49 |
| 9    | 1.55| 1.04 | 1.12 | 1.07 | 1.03 | 0.92 | 0.33 | 0.96 | 1.05 | 0.91 |
| 10   | 2.02| 1.15 | 2.02 | 1.28 | 2.03 | 1.09 | 1.70 | 1.00 | 1.72 | 2.34 |
| 11   | 2.43| 1.20 | 2.38 | 1.66 | 1.26 | 1.32 | 2.00 | 0.94 | 2.56 | 1.54 |
| Median | 1.81| 0.77 | 1.71 | 0.87 | 1.39 | 0.77 | 1.02 | 0.90 | 1.70 | 0.89 |

Table 6 shows the ratio between average summer and winter atmospheric deposition of the elements and PM for all sites. Significant differences for fluxes of AD of the most observed parameters were found between the summer and winter periods. Deposition of particulate matter and aluminum is significantly higher in the summer period with median ratio $S/W = 1.81$ and $1.7$. In the summer half of the year, there are better meteorological and climatic conditions for wind erosion and resuspension of particles from the soil horizon, road transport, agricultural and construction activities, also during the vegetation period, an increased incidence of organic debris is in the air. In winter, the deposition fluxes of PM are partially deprived of those effects. In winter seasons, an increased amount of components of AD, whose origin is in the energy-burning of fossil fuels on a local and regional scale is assumed. In the area of Košice, slightly higher or balanced values of deposition fluxes, in order Fe, Pb, Mn, Cr, Cd and Cu ($R_{S/W} = 0.77 -1.02$) were found in winter. Iron, manganese and chromium are typical elements of the earth's crust. For this reason, their higher fluxes of AD in the winter period are quite surprising. This fact can be explained by specific wind conditions in the studied area. In the winter period, in contrast to summer, there is an increased frequency of southern
wind with lower speeds which provides better conditions for sedimentation of particles in the north of the main source of emissions in the area. On the contrary, at sampling points 9, 10 and 11 located in the south of the ironworks, higher deposition values were recorded in the summer period, with a ratio of 1.04, 1.15 and 1.20 for iron and 1.07, 1.28 and 1.68 for manganese respectively, which supports this explanation. Also, the results of Pearson’s correlation analysis performed separately for the winter and summer periods confirmed this explanation. In the case of zinc ($R_{SW} = 1.39$) and arsenic ($R_{SW} = 1.70$), 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), also at station No. 5. The statistical dependence between individual elemental and PM fluxes of AD was determined separately for both, winter and summer periods by Pearson’s correlation analysis. The calculated coefficients are summarized in Table 7. Positive values of correlation coefficients were found for all monitored parameters. The highest values of correlation coefficients ($r = 0.82$ to $0.96$) were calculated for elements whose dominant source are technologies of ironworks, namely iron, manganese, chromium but also for aluminum and particulate matter. The relatively high values of the correlation coefficients were calculated for these elements with Pb ($r = 0.45$ to $0.75$), Zn ($r = 0.39$ to $0.80$) Cu ($r = 0.42$ to $0.60$), As ($r = 0.42$ to $0.63$) and Cd ($r = 0.34$ to $0.58$). A significant correlation value was found between zinc and cadmium ($r = 0.54$ to $0.70$). Higher values of correlation coefficients were calculated for the winter period in most cases.

Table 7. Pearson’s cross-correlation coefficients between fluxes of elements and PM, 

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a) Fe 0.96 0.92 0.94 0.75 0.54 0.53 0.86 0.52 0.58  
0.88 0.93 0.71 0.67 0.47 0.82 0.53 0.63  
0.88 0.65 0.45 0.42 0.79 0.43 0.46  
0.80 0.54 0.58 0.92 0.58 0.47  
0.41 0.57 0.78 0.70 0.38  
0.13 0.39 0.52 0.63  
0.66 0.27 0.30  
0.57 0.39  
0.33  

b) Fe 0.89 0.80 0.84 0.46 0.65 0.53 0.79 0.45 0.55  
0.80 0.94 0.41 0.75 0.58 0.80 0.44 0.47  
0.71 0.39 0.68 0.60 0.66 0.34 0.57  
0.42 0.64 0.52 0.90 0.48 0.41  
0.39 0.42 0.40 0.54 0.33  
0.36 0.45 0.57 0.49  
0.05 0.61 0.28  
0.41 0.36  
0.39
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Atmospheric deposition analyzes showed that more than 99% of the iron is bound to the insoluble fraction of AD. In addition to dust particles, it has a high degree of correlation with other elements that originate mainly in emissions from ironworks, such as manganese, chromium, but also zinc, and lead. AD of iron also shows a rapid decrease with increasing distance from the emission source. For these reasons, iron is the most suitable indicator of the origin of dust particles emitted from the emission sources of ironworks in the monitored area. The calculated impact of sources of ironworks on the deposition of Fe in the area was built on these facts. The values from the most loaded site 9 which is located in the vicinity of the ironworks with the insignificant impact of other sources were used [18,19]. The average percentage of Fe deposition from PM at site No. 9 was taken as the basis 100% ($B_{100\%}$) after deduction of the regional background of iron deposition (AD_{Fe Background}).

$$B_{100\%} = \frac{(AD_{Fe Site No.9} - AD_{Fe Background})}{(AD_{PM Site No.9} / 100)}$$  \hspace{1cm} (1)

The average values of iron deposition from the area of Krompachy, Slovakia (7 sites) obtained by using the same methodology in the summer ($1200 \, \mu g.m^{-2}.day^{-1}$) and winter ($600 \, \mu g.m^{-2}.day^{-1}$) periods were used as a background [16]. Iron in the Fe$_2$O$_3$ form was taken in the calculation for correction of
PM deposition. The corresponding values from the other sites were compared with the result of this calculation. In Table 8 the calculated average percentage share of emission sources from iron and steelworks on the AD of Fe fluxes at the individual sites is shown. There are significant differences between the summer and winter periods were found. The share of emission sources of iron and steelworks on the Fe fluxes at the urban sites (1- 6) was calculated in the range from 17.5 to 22.3% in the summer period, but up from 40 to 61 % in the winter period.

Table 8. The average share of emission sources of iron and steel works on the Fe deposition fluxes at the individual sites for summer and winter [%].

| Site | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|------|---|---|---|---|---|---|---|---|---|----|----|
| Distance [km] | 13.4 | 10.7 | 16.3 | 15.1 | 12.3 | 10.4 | 8.6 | 8.5 | 3.6 | 5.5 | 9.0 |
| Summer | 22.3 | 21.1 | 18.3 | 17.5 | 21.5 | 21.7 | 32.8 | 27.3 | 95.3 | 84.9 | 34.9 |
| Winter | 51.2 | 50.8 | 40.7 | 61.1 | 45.6 | 55.1 | 86.0 | 63.5 | 96.6 | 91.2 | 51.7 |

Figure 2. The share of emission sources of iron and steel works on the Fe deposition fluxes in depending on the distance sampling sites

In winter, this share was more than doubled. The share decreases proportionally with increasing distance as illustrated in Figure 2. The lowest portion was found at the furthest station No.3, the highest share at the sites located closest to the ironworks. Concerning the composition of emissions from ironworks, iron is their major component and also of atmospheric deposition of PM. It can be assumed that this specified share of the ironworks sources on deposition is not only valid for Fe but also for PM and other components fixed mainly to particles produced from these sources.

5. Conclusions

Elemental and PM deposition fluxes at different sites in the study area revealed significant differences in terms of spatial, temporal and seasonal variations, depending mainly on the locations of the sites, distances to emission sources, different activities and meteorological parameters. Detailed analysis of AD showed that in addition to Fe, Mn, and Cr, the ironworks complex is also a source of dust particles, aluminum and other observed elements in descending order of lead, zinc, copper, arsenic and cadmium. The average Fe deposition at urban stations in Košice was 2-3 times higher, compared with other urban areas. The very high values of deposition of iron, manganese and the over-average deposition of chromium, were measured mainly at sites near the ironworks. The impact of emission
sources of iron and steelworks on the fluxes of iron at the urban sites in winter was more than doubled portion compared to the summer period.

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