Statistical Evaluation and the Nature of the Deposited Dust of the Residential Agglomerations of the City Košice*

K. UHRINOVÁ, K. FLÓRIÁN, and M. MATHERNY

Department of Chemistry, Faculty of Metallurgy, Technical University of Košice, SK-042 00 Košice
e-mail: mikulas.matherny@tuke.sk

Received 25 June 2004

It is shown that preferentially the evaluation of the fluctuation of the mass of dust and the individual determined minor and trace elements was accomplished. Subsequently the correlation between the individual elements and the amount of dust was studied. The most frequent and well-correlated elements with the dust were Fe, Mn, and Ti. The rest of trace elements have variable character and create the trace element background of the dust.

Conventionally, the atmosphere pollutants are classified into three groups: the emissions, the immissions, and the deposited pollutants [1]. The deposited part of the atmospherical dust contaminates the whole area of the residential agglomerations. It contains both inorganic (*ca.* 70—95 %) and organic (5—30 %) substances. The most frequent main and minor elements of the gravitation dust sediments in the given region, with exception of C and SiO_2, are Fe, Mn, and Ti. The elements Fe and Mn penetrated into the atmosphere by the whirl of anthropogenic dust particles, and by frequent thoroughfares and industrial activities. The Ti compounds enter the atmosphere by atmospherical immissions (transports) from the large-size agricultural activities. Pb is a toxic element and enters the atmosphere from the exhaust gases of petrol engines [2]. The rest of the trace elements (Co, Cr, Cu, Ni, Pb, Sn, V, and Zn) has a variable origin and creates the trace element background of the dust [3, 4]. The high toxic elements As, Be, Cd, and Hg were not determined, because their concentration in dust samples was about two magnitudes lower than their limit of detection ($\bar{w}(\mathrm{X})_\mathrm{L} \approx 0.05$ ppm).

The Košice valley has a funnel-shaped form (Fig. 1). In the N part it is very tight (*ca.* 2—3 km), in the middle part it is widened (5—7 km), and in the S part it is spread in the lowland. In consequence, it is the wind speed and its fitfulness in the northern part is the highest, in the middle part of the city it is significantly lower, and in the southern part it has a characteristic low and laminar character [5].

By the evaluation of changing of the amount of dust it is necessary, except the amount itself of sediment dust part, to take into account the meteorological [1] and geographical conditions of the tested residential agglomeration [6]. The months November till May are denoted with the prevailing N winds (*ca.* 67 %). On the opposite side, the months July till October are marked by stable N and S winds. The unequivocal N winds clean the Košice valley from the pollutants because the northern part of East Slovakia is free from extremely high pollutants producing emission sources. On the other hand, the S winds bring pollutants of the soil erosion from the southern areas, which are marked in these months by intensive agricultural activities. The concentration of the surface soil elements in the summer season is highly enriched. Near Košice, about 14 km westward from the city cen-

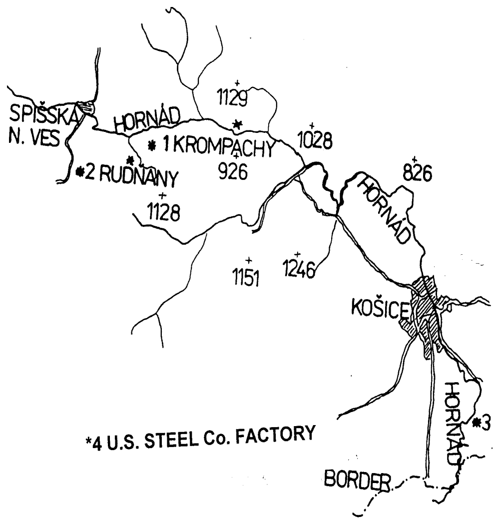

Fig. 1. Map of the wide surrounding of the city Košice. 1. and 2. Nonferrous metallurgical factories, 3. incinerator factory, 4. steel factory.

*Presented at the NATO Environmental Conference, Gödöllő, Hungary, April 2003.

tre, the ironworks and steelworks U.S. Steel Co. is situated. In addition, in this region the amount of W and E winds is minimal (*ca.* 7 %), this factory contaminates the city Košice with Fe and Mn oxides only by atmospheric diffusion processes. Their amount is significantly lower than the general amount of directly transported dustiness pollutants. Commonly, the dust is not toxic but its many years influence on the vegetation and also on living objects may possibly cause permanent unfavourable consequences on the environment. Therefore, it is necessary to observe not only the amount but also the chemical character of the dust [7].

As conclusion it is possible to confirm that the most significant pollutant of the atmosphere is the deposited part because this pollutant represented the main amount of the total dust of the residential atmosphere. The deposited part of the dust concentration is caused by the anthropogenic activities, especially in the residential agglomerations on the ground of the raise of urban dust, persistently crushed. By this procedure the concentration of the airborne dust is enhanced. Herewith the negative influence of the atmospherical dust is increased. Therefore it is primarily necessary to follow not only the amount but at the same time also the chemical character of the deposited dust.

EXPERIMENTAL

The atmosphere of the residential agglomeration of Košice was patterned during two-year period (2001—2002). Samples were taken according to the DIN standardized Bergerhoff method [8]. The complex wet and solid samples were evaporated by 100 ℃, and dried by 150 ℃. Dry samples were analyzed by the DC-OES method [9, 10]. Experimentally, the monthly mass fluctuation of the gravitation dust sediments, the mass of the minor elements Fe, Mn, and Ti, and also the trace elements Co, Cr, Cu, Ni, Pb, Sn, V, and Zn were followed. For all studied elements the limit of detection and the relative standard deviation of concentration determination are given in Table 1. The content of Ag, Bi, Mo, Sb, and W was mainly under the average limit of detection ($\bar{w}(\mathrm{X})_\mathrm{L} \approx 0.1$—$0.05$ ppm), and therefore their determination is very problematic.

Table 1. Comparison of the Main Validation Parameters of the Used DC-OES Method

Element (X)	Limit of detection $\bar{w}(\mathrm{X})_\mathrm{L}$/ppm	Relative precision $s(w)_{\mathrm{X,r}}$/%
Main and minor elements		
Fe	14.0	8.3
Mn	4.2	6.3
Ti	26.0	8.4
Trace elements		
Co	0.3	10.7
Cr	7.6	5.8
Cu	1.1	16.3
Ni	8.4	7.8
Pb	5.4	13.7
Sn	11.0	6.4
V	0.7	5.5
Zn	14.0	13.6

RESULTS AND DISCUSSION

In Figs. 2*a* and 2*c* are given the values of total monthly amounts m_i of dust in t km^{-2} year^{-1}, but the monthly amounts of elements (Figs. 2*b* and 2*d*) are given in kg km^{-2} year^{-1}. It is evident that the interpretation of this data cluster requires statistical treatment. The change of the total monthly amount of dust for the years 2001 till 2002 is demonstrated by differential histograms in Fig. 2. These diagrams represent the difference Δm between the arithmetical mean value $\overline{m}$ and the absolute monthly sediment value m_i.

On the given histograms it is possible to distinguish two marked different year periods. The first one begins in November and lasts till May of the next year and is marked by characteristic minimum of dust. In this period mostly N and NE winds (*ca.* 67 %) prevail in the Košice valley. These winds empty the valley from the pollutants. The second year's period, from June to October, is marked by evident maximum of deposited dust. This period is marked also by the equality of N and S winds. The southern part of Košice valley has a flat character and is marked by intensive agricultural activity, namely with the erosion of the soils. Therefore, in this period the deposited dust is increased.

The monthly fluctuations of the amount of separate elements are significantly different with the exception of the element Fe (Fig. 2*d*). The decrease of the dust in the year 2002 is remarkable also by the decrease of the element amount of Fe. The similarity of the amount of Mn and Ti with the amount of dust is already less characteristic. But the amount of Ti in the dust was nearly constant. The other trace elements show specific distribution behaviour. The distribution of Cu and Zn is similar but at the same time relatively irregular because the main part of these pollutants penetrates in the atmosphere north-west of Košice in the river-basin of Hornád from the emissions of pyrometallurgical factories Rudňany and Krompachy. Therefore, it is less conditioned by meteorological factors. The amount of Cr, and also other trace elements, formed the trace-element background of the pollutants of the atmosphere and showed not desirable regularities.

The main aim of the statistical evaluation of the experimental data was directed to the clarifying of the coherence between the dust amount and its element components. The framework of this evaluation was primarily directed to the determination of the correla-

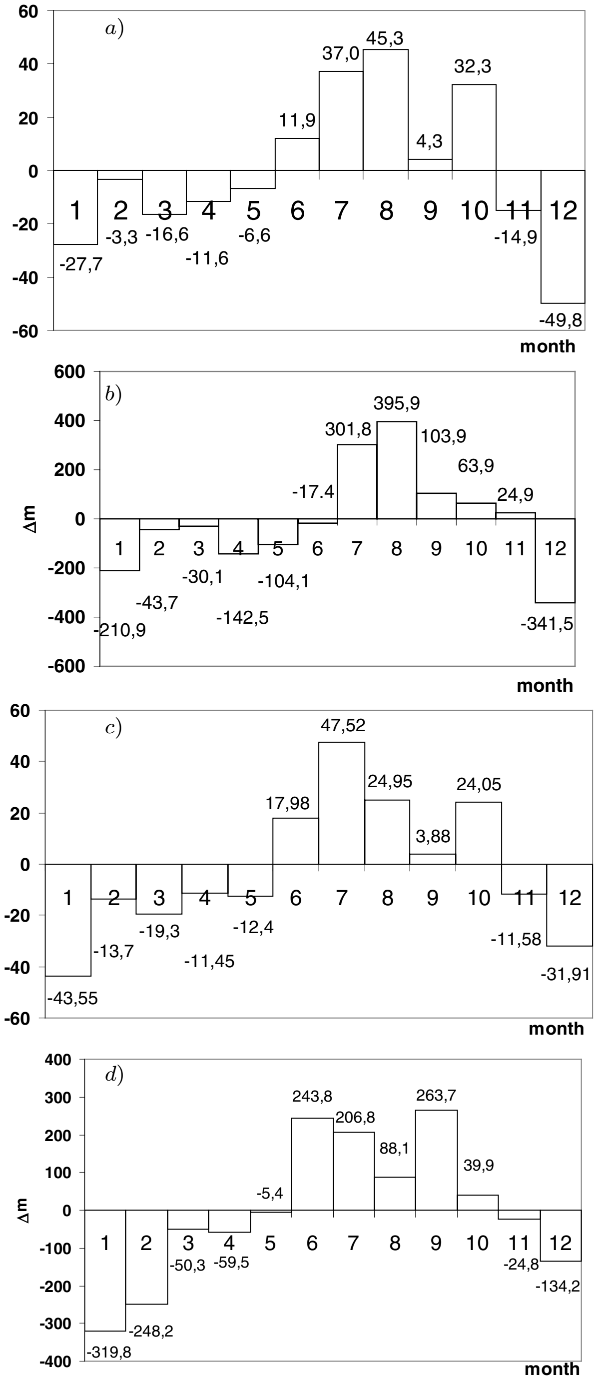

Fig. 2. Differential histogram of the monthly change of: *a*) the gravitation dust sediment amount m(G.D.S.) in the year 2001, dimension on the y-axis: (t km^{-2} year^{-1}), $\overline{m}$ = 71.3 (t km^{-2} year^{-1}), *b*) the Fe amount (m(Fe)) in the year 2001, dimension on the y-axis: (kg km^{-2} year^{-1}), $\overline{m}$= 424.1 (kg km^{-2} year^{-1}), *c*) the gravitation dust sediment amount (m(G.D.S.) in the year 2002, dimension on the y-axis: (t km^{-2} year^{-1}), $\overline{m}$ = 59.95 (t km^{-2} year^{-1}), *d*) the Fe amount (m(Fe)) in the year 2002, dimension on the y-axis: (kg km^{-2} year^{-1}), $\overline{m}$ = 362.1 (kg km^{-2} year^{-1}).

tion between the amount of dust and the amount of selected elements during two-year period. Additionally,

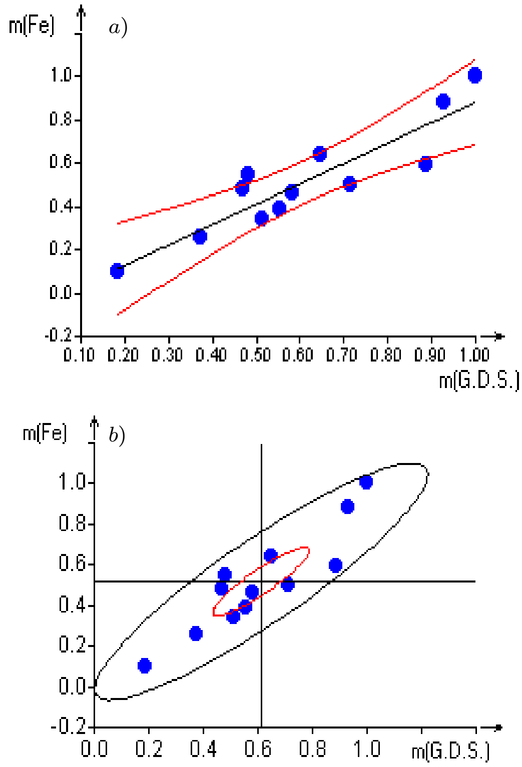

Fig. 3. Regression diagram (*a*) and scatter diagram (*b*) with confidence lines of the combination of Fe amount (m(Fe)) and the total amount of dust (m(G.M.S)).

the nearness of the tolerance lines to the orthogonal regression lines was fixed. This phenomenon marked the measure of precision of the folding of orthogonal regression line. Finally, the character of the counter diagrams was evaluated and the distribution character of both the compared values was highlighted (Fig. 3).

The detailed correlation-regression analysis of monthly amounts of the individual elements for the years 2001 and 2002 provides following improvement of the studied problems. For the statistical treatment the QC-Expert software of the TriloByte was used [11]. The correlation of the amount of Fe and the amount of dust is also conditioned by the above defined year periods. Under the dust minima, under the prevailing N winds, the correlation for the two-year period is considerably high and the value of correlation coefficient increases to $r = 0.71$. On the other hand, the correlation of Fe with the dust under the equivalent N and S winds is low, $r \approx 0.50$, and the value of the orthogonal regression coefficient is approximately also low, $w_{\mathrm{orth}} \approx 0.45$. The scatter diagrams fulfilled the elliptical shape but simultaneously the confidence limits are very far from the regression line. This phenomenon is caused by the S winds, which diluted the original dust concentration of the Košice valley and have different dust character in comparison with the character of dust of N winds system. Namely, the system of S winds contains a significant part of clay minerals with

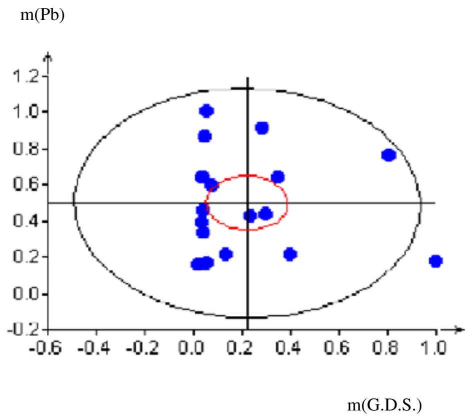

Fig. 4. Scatter diagram of the combination of Pb amount (m(Pb)) and the total amount of dust sediment (m(G.D.S.)).

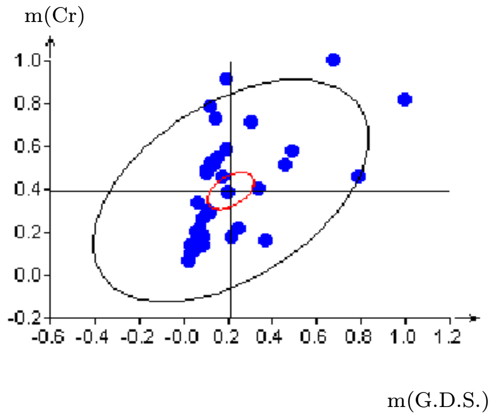

Fig. 5. Scatter diagram of the combination of Cr amount (m(Cr)) and the total amount of dust sediment (m(G.D.S.)).

Al, Ca, and Ti components. The confidence limits are in tight-fitting nearness of the regression lines. That means that the generation of Fe in the atmospheric dust is also in good correlation with the generation of the dust. This unambiguous dependence for Mn and Ti was not confirmed. The values of correlation coefficients for the pairs Mn/dust and Ti/dust were confirmed only on the level $r \approx 0.56$. Currently were obtained also lower values of regression coefficients. The scatter diagrams come near to the round diagrams. Lastly, it is necessary to state that by other trace elements the required correlation and regression are not confirmed. In the case of the combination Pb/total dust this fact is given by the different generation of Pb and the dust (Fig. 4). Namely, the amount of Pb component in the atmosphere of residential agglomerations is given by the amount of produced exhausts of motor engines with Pb antiknock fuel additives and not with the original dust. The regression line is running parallel with the axis of dust. Finally, the ratio mCr/m total dust (Fig. 5) in the years 2001 and 2002 confirmed that this trace element is not at all correlated with the amount of dust and forms the trace elemental background. Even in the year 2001 negative correlation between the amount of Cr product and the observed dust was still reached.

CONCLUSION

This article solves firstly the problem of the fluctuations of dust in the residential agglomeration of Košice. This residential agglomeration is situated in the East Slovakia and it is the dominant city with 350 000 inhabitants. In relationship with the problem of dust contamination, the problem of the change of chemical character of this dust is discussed. The amount of the dust and the product of the general dust concentration changed in this region in the one-year period regularly and proportionally. From December till the end of June, when the N and NW winds are prevailing, the dust is low, about 45 up to 60 t km^{-2} y^{-1}. On the other hand, in the season from July to the end of November, when the S winds are prevailing, the dust concentration clearly increased to 95 up to 110 t km^{-2} y^{-1} values. The given dust concentration data do not exceed the limit of WHO, which is 150 t km^{-2} y^{-1}. The winds in this region preferentially conditioned the transport conditions of general dust from the border parts of the agglomeration to the middle part.

The amount of metal compounds, mainly oxides, in the dust is expressively different. The abundance of Fe in the studied sediments is the highest and is well correlated with the total amount of dust. Similarly, Mn and Ti reached expressive correlations but not so high. From the aspect of heavy metals high Pb amounts are reached. The occurrence of Cu and Zn did not correlate with the amount of dust. Probable emission sources of these elements are the pyrometallurgical factories in the northwestern part in the river-basin of Hornád. The element Cr and the other trace elements, the amount of which in dust is low, are not in good correlation with the total amount of dust.

Acknowledgements. This work was supported by the Slovak Grant Project No. 1/0214/03 and Slovak/German International Cooperation Project No. 01/021-2003. The authors feel obliged to express their gratitude for this support. The authors express their gratitude to Professor Dr. M. Meloun from the Pardubice University and Eng. K. Kupka from the TriloByte for the use of software QC-Expert.

REFERENCES

1. Junge, Ch. E., *Air Chemistry and Radioactivity.* Academic Press, New York, 1962.
2. Flórián, K., Matherny, M., and Pliešovská, N., *Trans. Techn. Univ. Košice 3*, 143 (1993).
3. Matherny, M., Balgavá, V., and Einax, J., *Chem. Pap. 48*, 95 (1994).

4. Ure, A. M. and Davidson, C. M., *Chemical Speciation in the Environment.* Blackie, London, 1985.
5. Güven, K. and Güral, T., *Atmospheric Environment 31*, 3985 (1997).
6. Matherny, M., *Proc. 6th Conf. Environ. Mineral. Process,* p. 119. Ostrava, 2002.
7. Malisa, H. and Robinson, J. W., *Analysis of Airborne Particles by Physical Methods.* CRC, Palm Beach, 1979.
8. VDI/DIN, *Handbuch Reinhaltung der Luft.* Vol. *4*, Part 2. Beuth Verlag, Berlin, 1996.
9. Flórián, K. and Pliešovská, N., *Acta Chim. Hung. 103,* 301 (1980).
10. Flórián, K., Gálová, M., Koller, L., Krakovská, E., Lux, L., Matherny, M., Nickel, H., and Pliešovská, N., *Acta Chim. Hung. – Models in Chemistry 129*, 611 (1992).
11. Kupka, J., *QC-Expert 2.5 Statistical Software.* Trilo-Byte, Pardubice, 2002.