

## Quality of the Atmospherically Dustiness of the City Košice and Surrounding

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**Abstract.** The atmospherically dustiness has three origins: emissions dustiness, the imissions, dustiness and the last form is the deposited part. The deposited dustiness formed the gravitation dust sediments with the diameter higher as 10  $\mu\text{m}$ . The given particles sediment spontaneously. This part of atmospherically dustiness was in the residential agglomeration of the city Košice patterned during the year periods 2000 till 2002. The dust samples were taken according to the DIN standardized Bergerhoff method. Finally it was necessary to observe not only the total amount of gravitation dust sediments, but also their chemical composition

Firstly was evaluated the changing of the monthly amount of the gravitation dust sediments. Furthermore the evaluation of the experimental results was directed towards to the study of correlations-regressions phenomena between the monthly amount of gravitation dust sediments and the individual element amounts. As a result can be stated that the most frequented and well-correlated elements with the amount of dust particles are the elements Fe, Mn and Ti. The elements Cu and Zn enter in to the atmosphere from the exhaust of pyrometallurgically factories in the basin of the river Hornad (Rudňany, Krompachy). The concentration of Pb is high and this element enters in the real time in the atmosphere from the exhaust gasses of petrol engines. The rest of trace elements like Co, Cr, Ni, Sn, and V possess a variable character and create the trace elements background of the atmospherically dustiness.

**Key words:** Atmospherically dustiness, gravitation sediments, statistical evaluation, correlation, regression

### Introduction

The atmospherically dustiness from the standpoint of its genesis consist of three components: the dustiness indicated by the emitted dust of emission point sources, the transported dustiness bounded with the distant imissions, and finally the deposited, spontaneous sediment dust particles (Junge 1962). On the genesis of given dustiness forms beside the source characters, meteorological and geographical parameters the main influence has the idealized particle size (Junge 1962, Malisa & Robinson 19779, Einax et al. 1991). The particles with diameter less as 1  $\mu\text{m}$  not are to able spontaneous sediment generally. On the opposite side the particles with diameter higher as 10  $\mu\text{m}$  sediment always spontaneously. The particles with diameter between 1 to 10  $\mu\text{m}$  sediment only partially and this sedimentation is mainly given by the interaction of their chemical character and meteorological conditions (fog, rain, snow). This phenomenon is called mainly as: washing of the atmosphere. The deposited part of atmospherically dustiness creates the gravitation dust sediments (further only dust). Airborne dust particles are also partially shaped by the anthropogenic activity in the residential agglomerations. That ones elevate the atmospherically toxicity.

The genesis of the predominant elements (C as graphite,  $\text{SiO}_2$ , Ca, and Mg carbonates), subsidiary elements (Al, Fe, Mn, Ti) and the whole group of different trace elements are very dissimilar. While the surface elements (Al, Ca, Mg, Ti) penetrated in the atmosphere by the ero-

sion of soils, the other common elements (C, Si, Fe, Mn) and the heavy metal elements come partially from the emissions of industrial activities (Ure & Davidson 1985).

### Experimental part

The dust was sampled by the Berghoffer method (VDI/DIN 1996) in glass pots. This pot was during winter period filled by methylalcohol, and in the other year periods only with distilled water. By these additives the powder particles was stabilized. The obtained mixture of rain and solid particles was firstly at 105 °C evaporated and finally at 125 °C dried to the constant weigh. The chief sampling station was situated in the middle part of the city Košice on the top of the main building of Technical University. The auxiliary sampling stations are in the wide surrounding of Košice (Fig. 1): in the middle part of city Prešov (36 km western), and the villages Dargov (31 km eastern), Moldava (29 km western), and Čaňa (20 km southern). The sampling period was restricted on the years 2000, 2001 and 2002 with monthly interval. The amount of the sampled dust is expressed in  $\text{t km}^{-2} \text{ year}^{-1}$  units. Opposite the individual elements amount in dust was expressed in  $\text{kg km}^{-2} \text{ year}^{-1}$ .

In this powder samples was from the group of common and surface elements only the concentrations of Fe, Mn, and Ti determined. The predominant elements (C, Si, Ca, Mg) were not followed because the used analytical method was optimized for the concentration range of subsidiary and trace elements. For the concentration deter-

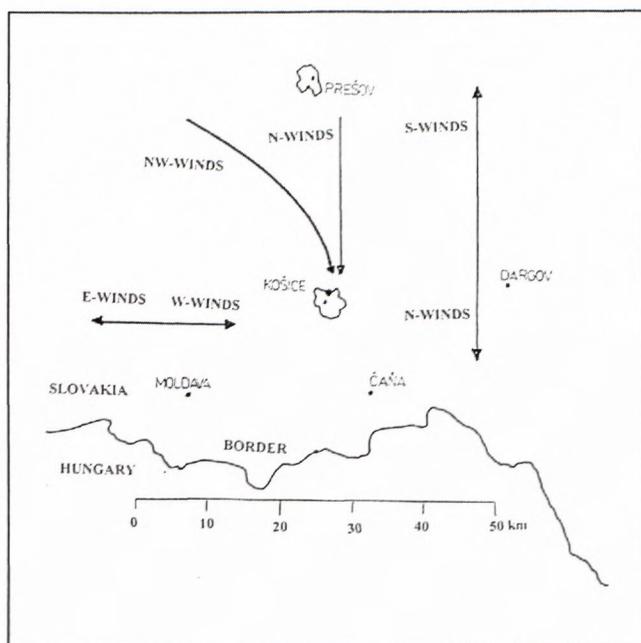


Fig. 1. The sampling stations in East-Slovakia

mination of chosen subsidiary and trace elements (Co, Cr, Cu, Ni, Pb, Sn, V and Zn) was used the optimized method with excitation in DC arc (Flórián et al. 1992). The concentration of the light volatile elements (Ag, Bi, Mo, and Sb), and the high toxic elements (As, Be, Cd, Hg) was not determined because their concentration level was clear low as their analytical limits of detection ( $\bar{m}(X)_L \approx 0.02$  ppm). From the environmental standpoint mentioned light volatile and toxic elements in the given region are not typical pollutants. By the statistical evaluation in the attention of outstanding comparability were the "eigenvalues" applied.

## Results and Discussion

The complexes exploratory statistical analysis of the data of dust amount was realized with the software QC Expert 2.5 (Kupka 2002). These calculations built mainly on the calculation of arithmetical mean  $\bar{m}$ , the median  $\tilde{m}$ , the modus  $\hat{m}$  and the half sum  $m_p$  values and the testing of the asymmetry, the excess, the homogeneity and normal distribution of experimental values.

The comparisons of the data from the five sampling stations (Tab. 1) confirmed that the amount of the dust is homogenous distributed and this distribution have normal Gaussian character. In the Fig. 2 is given the example of the most characteristic early-optimized histogram, the distribution curve and the round-like diagram for the sampling station Čaňa. The conformity the real functions with the theoretical is very high what consideration the above confirms. But the characteristic values for the sampling station Moldava (Fig.3 and Tab. 1) demonstrate the least advantageous example. This consideration demonstrates mostly the different courses of the histograms and the round-like diagrams. The similarity of the computed

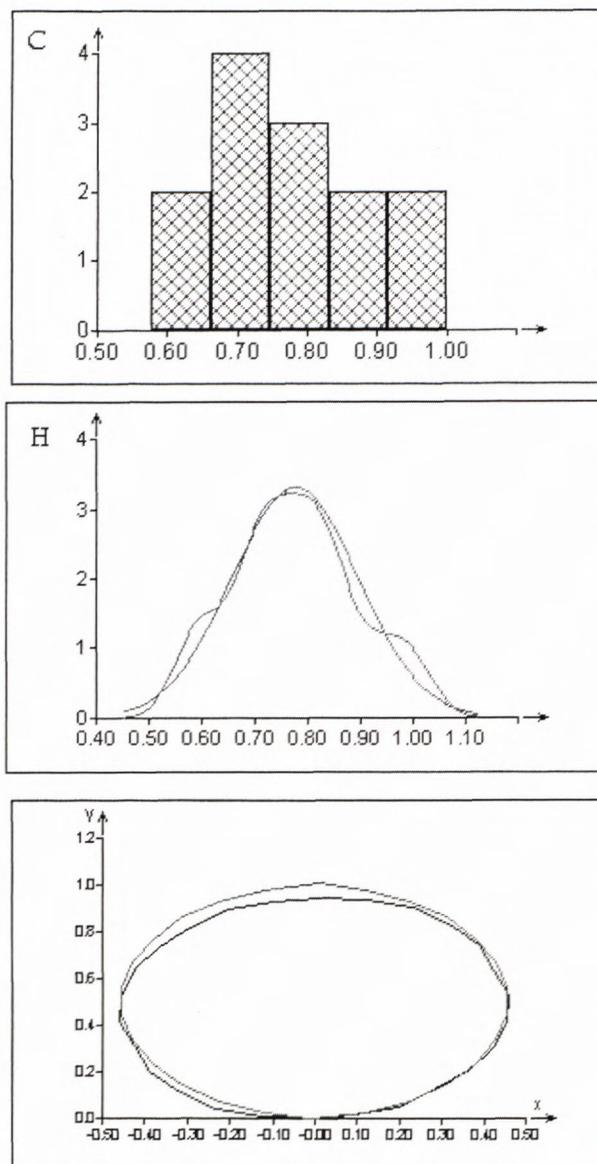


Fig. 2. The histogram, the distribution curve and the round-like diagram of the dust amount in Čaňa, C - multiplicity, H - density

data for the sampling stations in Košice, Čaňa and Prešov (Fig. 1), which is the direction of the prevailing N → S winds (ca 67 %), is most expressive.

The detailed analysis of the statistical properties of the dust from Košice showed the following results. The fluctuation of the total amount of gravitation dust sediment in the years from 2000 till 2002 is illustrated in the differential histograms (Fig. 4) of the  $\Delta m$  values. This present the difference between the monthly measured values  $m_i$  and the annual arithmetical mean value  $\bar{m}$ .

$$\Delta m = m_i - \bar{m}$$

It is possible to distinguish two years period in the given histograms. The first period, from November till May of the next year is demonstrated in all observed tree years with marked dustiness maximum. This conclusion confirmed that the meteorological conditions have domi-

Table 1: Evaluated statistical parameters of the dust amounts

Sampling stations	$\bar{m}$	$\tilde{m}$	$\hat{m}$	$m_p$	Asymetry	Exces	Homogenity	Normality
Košice	0.58	0.57	0.55	0.57	akcepted	akcepted	akcepted	akcepted
Čaňa	0.78	0.77	0.76	0.77	akcepted	akcepted	akcepted	akcepted
Prešov	0.63	0.64	0.65	0.64	akcepted	akcepted	akcepted	akcepted
Dargov	0.71	0.71	0.71	0.71	akcepted	akcepted	akcepted	akcepted
Moldava	0.66	0.70	0.77	0.66	not akcepted	akcepted	akcepted	akcepted

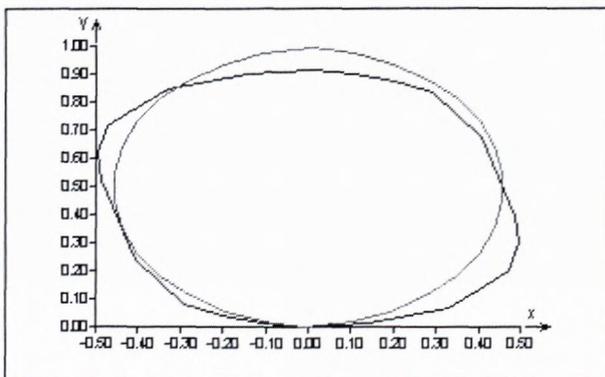
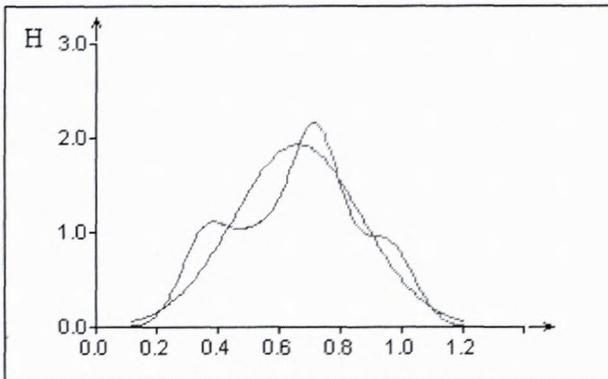
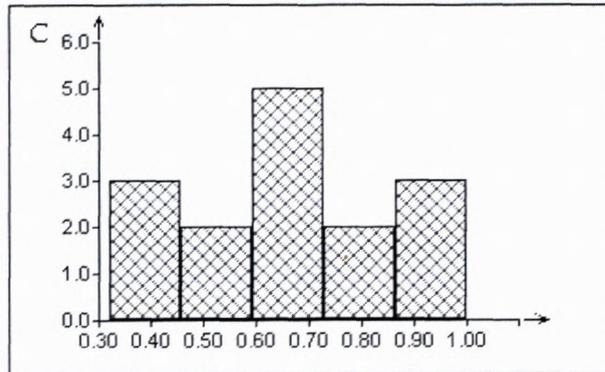


Fig. 3. The histogram, the distribution curve and the round-like diagram of the dust amount in Moldava, C - multiplicity, H - density

nant character in this case. In this period prevailed in all East-Slovakian regions the N and NW winds (67 %). These winds cleans the region from the pollutants because northern from Prešov are nothing expressive pollution sources which contaminated the atmosphere with inorganic products. The second period, from June till Oc-

Tab. 2. The values of correlation and regression coefficients

Elements in dust	Correlation coefficients		Slopes	
	$r_{\min}$	$r_{\max}$	$a_{\min}$	$a_{\max}$
Fe	0.78	0.91	0.87	1.0
Mn	0.32	0.71	0.33	0.92
Ti	0.17	0.88	0.18	1.0
Zn	0.22	0.78	0.24	0.93
Cu	-0.26	0.16	-0.25	0.23
Pb	-0.07	0.21	-0.08	0.28
Cr	-0.29	0.09	-0.27	0.12

tober, is in opposites position and it is marked with dustiness maximum. The N and S winds are in equality in this considered period. This winds are contemporary minimal (7 %) and therefore is their influence expressions less. The south part of the East-Slovakia has a lowland character with intensive agricultural activity. The intensive erosion of the soil causes the contamination of the atmosphere with the surface elements (Al, Ca, Mg, Ti). Only one artificial case (2000, August) from the regularity of the diversity of minimal and maximal dustiness was found.

The monthly fluctuations of the individual followed elements are enough different. The limiting values of correlation coefficients and the values of slopes of the counter ellipses, which present the regression lines, are listed in the table 2.

The most similarity of the distribution of Fe amount with the amount of dust is demonstrated in the Fig. 5. The average amount of Mn is about factor 8 to 10 lower. Therefore the monthly differences are also lower and the two different periods are not clear (Fig. 6). The similarity of Ti distribution with the distribution of precipitated dust particles is not so pregnant (Fig. 7). It is necessary to be aware that the geneses of Ti amount have another character as the other subsidiary elements.

The further trace elements have very element specific distribution character. The genesis of Cu (Fig. 8) and Zn (Fig. 9) elements is bounded on the emissions of pyrometallurgical factories in the Hornad river valley. The pollution and therefore also the element distribution of the atmosphere are conditioned by the campaigner character of the metallurgical production. This valley flow in the funnel shaped Košice valley and contaminate irregular the all-residential agglomeration. Lastly the amount of

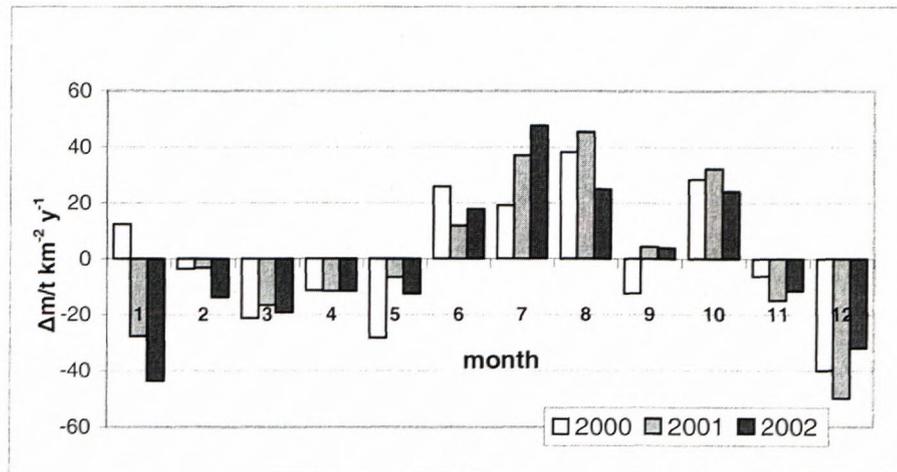


Fig. 4. Monthly swinging of the dust amount in the years 2000 till 2002 in  $t\ km^{-2}\ y^{-1}$  units.  $\bar{m}(2000) = 78.9$ ,  $\bar{m}(2001) = 71.3$ ,  $\bar{m}(2002) = 59.9$

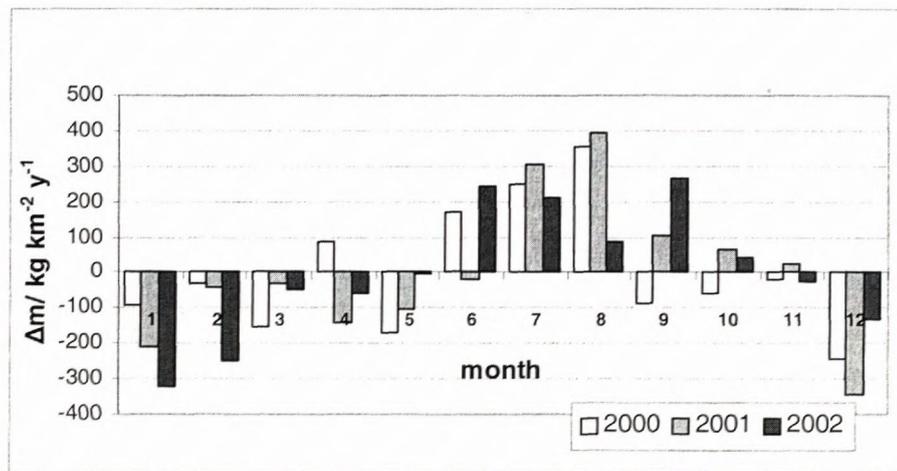


Fig. 5. Monthly swinging the Fe amount of dust in the years 2000 till 2002 in  $kg\ km^{-2}\ y^{-1}$  units.  $\bar{m}(2000) = 417.4$ ,  $\bar{m}(2001) = 424.1$ ,  $\bar{m}(2002) = 362.1$

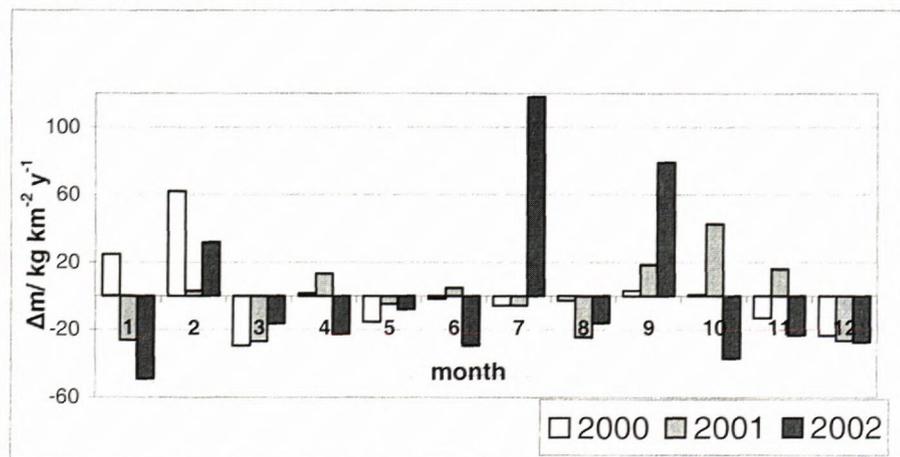


Fig. 6. Monthly swinging the Mn amount of dust in the years 2000 till 2002 in  $kg\ km^{-2}\ y^{-1}$  units.  $\bar{m}(2000) = 51.1$ ,  $\bar{m}(2001) = 42.6$ ,  $\bar{m}(2002) = 54.9$

Cr and the other followed trace elements is low, approximately 1 till 6  $kg\ km^{-2}\ y^{-1}$ . The distribution of the amount of Cr (Fig. 10) is without any regularity.

In continuation of the dustiness research, the correlation-regression analysis and the construction of the scatter diagrams was applied. In the first dustiness

period the correlation-regression analysis between the Fe amount and the amount of gravitation dust sediment (Fig. 11) shows high correlation ( $r = 0.91$ ) and also almost ideal regression ( $w = 0.99$ ). The courses of the confidence limits lines are very narrow to the regression line. The counter diagram was denoted as clear and narrow

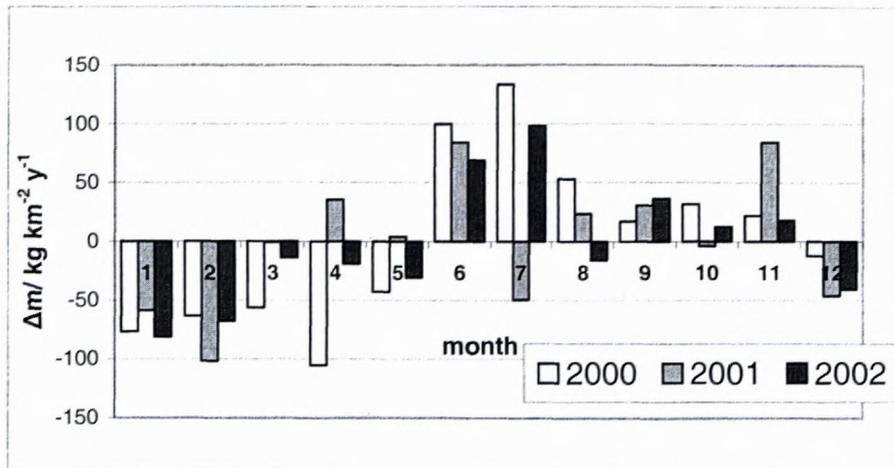


Fig. 7. Monthly swinging the Ti amount of dust in the years 2000 till 2002 in  $\text{kg km}^{-2} \text{y}^{-1}$  units.  $\bar{m}$  (2000) = 105.3,  $\bar{m}$  (2001) = 101.7,  $\bar{m}$  (2002) = 100.0

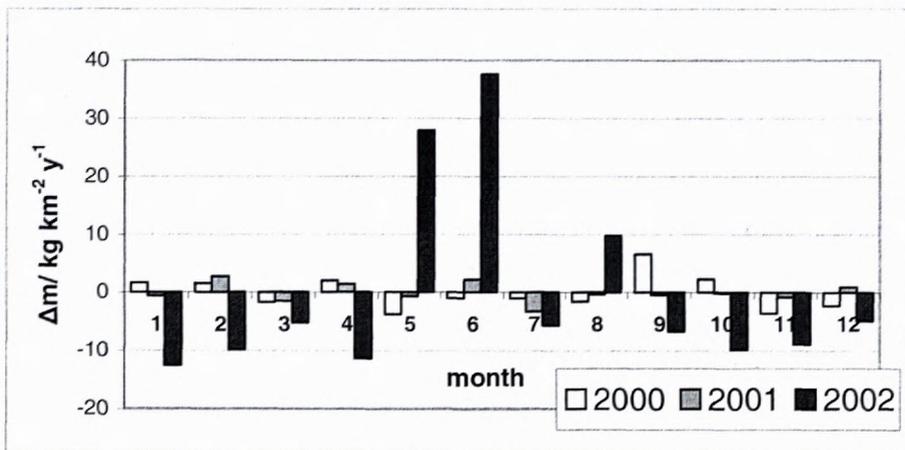


Fig. 8. Monthly swinging the Cu amount of dust in the years 2000 till 2002 in  $\text{kg km}^{-2} \text{y}^{-1}$  units.  $\bar{m}$  (2000) = 6.0,  $\bar{m}$  (2001) = 4.4,  $\bar{m}$  (2002) = 14.0

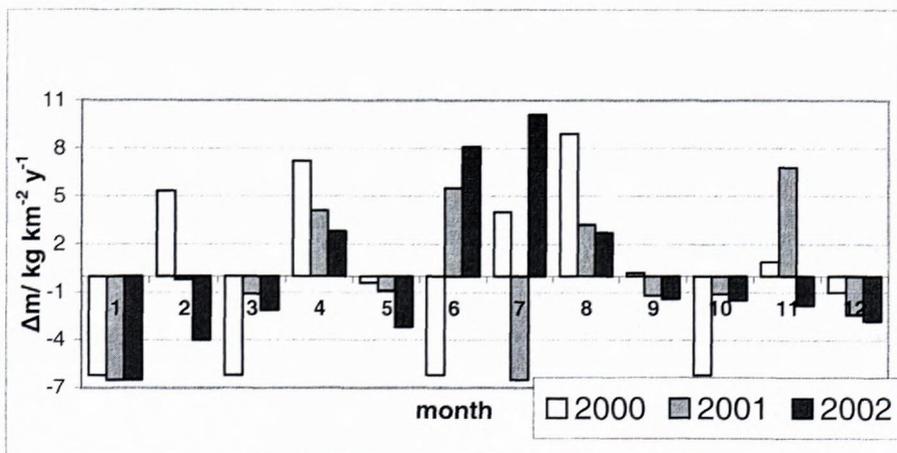


Fig. 9. Monthly swinging the Zn amount of dust in the years 2000 till 2002 in  $\text{kg km}^{-2} \text{y}^{-1}$  units.  $\bar{m}$  (2000) = 6.2,  $\bar{m}$  (2001) = 6.5,  $\bar{m}$  (2002) = 8.2

ellipse. These results confirmed that the genesis of Fe amount direct related with the total dustiness amount. In the second dustiness period under equivalent frequency of N and S winds the correlation expressively fall to the value  $r = 0.45$ . This worsen of the correlation was caused by the dilution of the atmosphere with S winds with amount of surface elements and changeable Fe amount.

Unequivocal dependence for the Mn and Ti amounts was found. Their correlation coefficients for the years 2000 till 2002 moved for the amount of Mn between the values  $\langle 0.32, 0.70 \rangle$  and for Ti between  $\langle 0.17, 0.88 \rangle$ . Contemporarily was confirmed a lower regression as by the Fe amount. The dependence for the amount of Cr (Fig. 12), which ire presents the clear trace elements, shows that

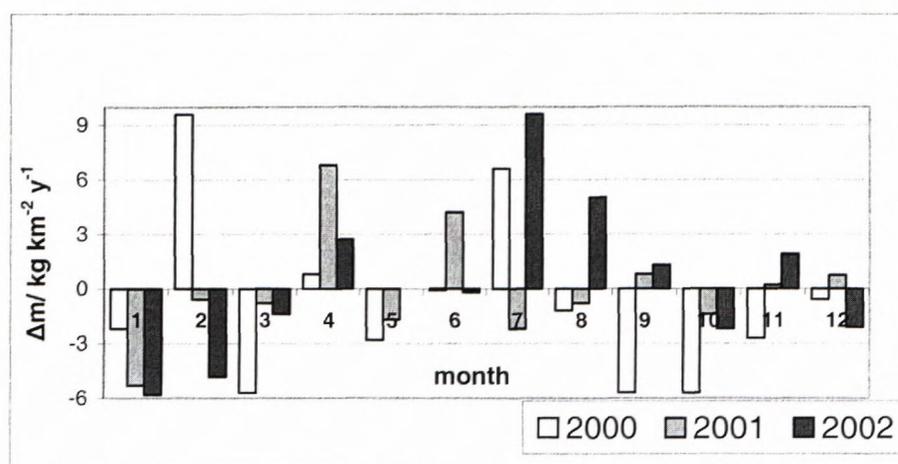


Fig. 10. Monthly swinging the Cr amount of dust in the years 2000 till 2002 in  $\text{kg km}^{-2} \text{y}^{-1}$  units.  $\bar{m}$  (2000) = 5.7,  $\bar{m}$  (2001) = 5.3,  $\bar{m}$  (2002) = 7.2

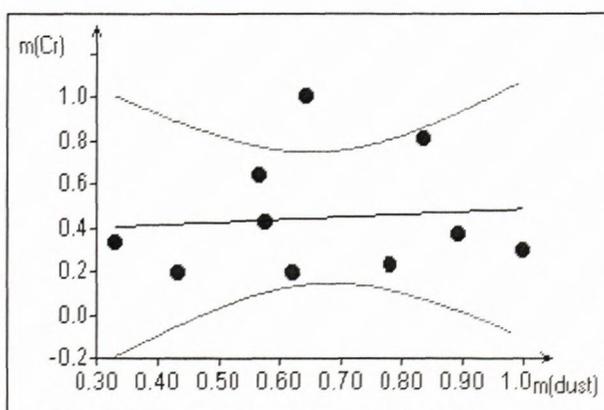
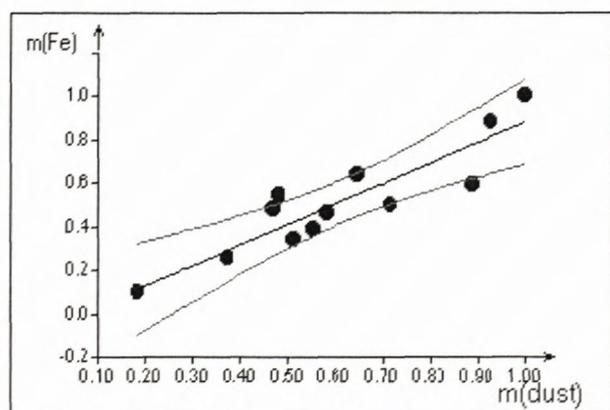
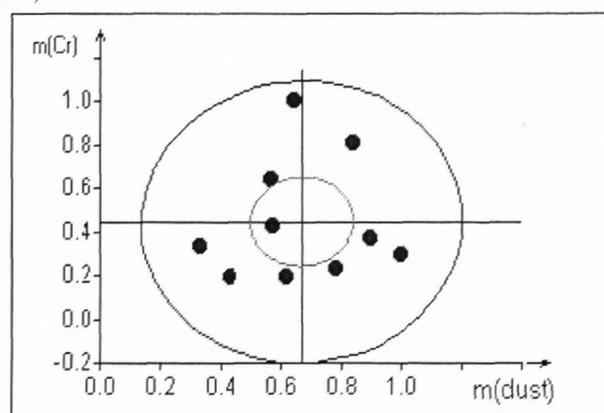
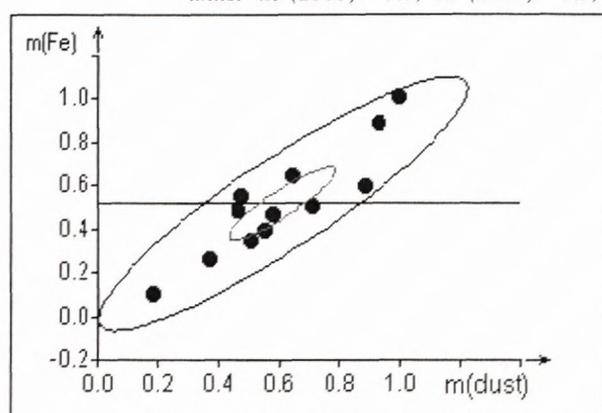


Fig. 11. The scatter diagram and the regression straight line for the Fe / dust amount ratio

Fig. 12. The scatter diagram and the regression straight line for the Cr / dust amount ratio

this element and the all member of this group of elements not correlated with the amount of the dust. That means that this group is formed only the element background of the atmospherically dustiness, and is present by not typical pollutants. Lastly it is necessary to discuss the behavior of Pb. This element presents in the residential agglomeration a specific problem. The amount of this element (Fig. 13) shows extremely low correlation and zero regression. This phenomenon is caused by the fact that its genesis is footed not in the general dustiness but primarily in the amount of Pb containing additives in the exhaust of motor engines.

## Conclusion

The validation of the dust fluctuation not only the total dust amount but also it is necessary take into accounts the predominant meteorological situations and the geographical abilities in the residential agglomerations and the given regions.

The N and S winds alternate in the funnel shaped region of the city Košice. The amount of W and E winds is irrelevant. These phenomena create two typical dustiness situations. The first case is characterized by prevailing N winds and is distinguished by the minimum of dustiness.

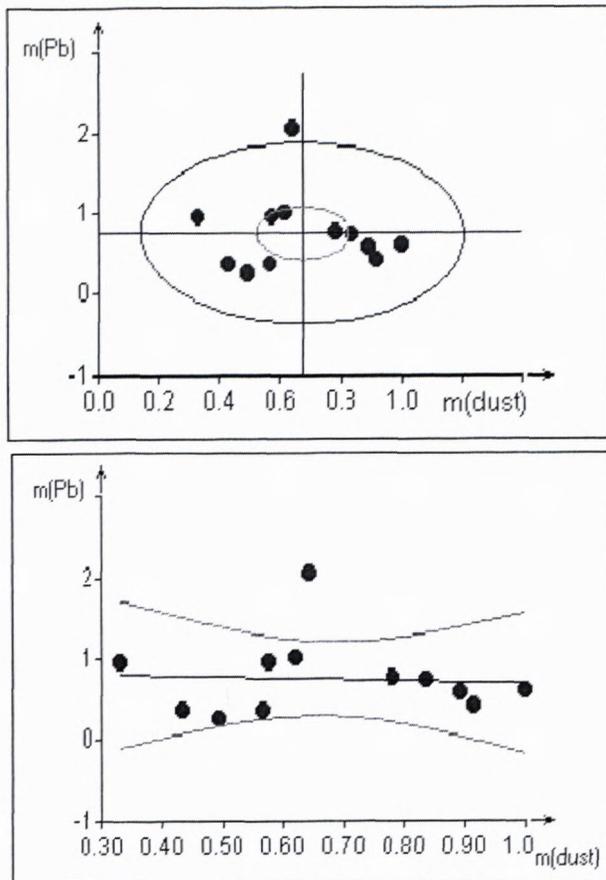


Fig. 13. The scatter diagram and the regression straight line for the Pb / dust amount ratio

The second case with balanced N and S winds is characterized by the maximum of dustiness. These phenomena is caused by the enhancing of the atmospherically dustiness with surface elements from the soil erosion in the southern part of the city Košice.

The amount of the components, mainly oxides and sulphates of metallic elements, is in the dust very variable. The subsidiary elements Fe, Mn, and Ti come mainly from the geological substratum and present the constant highest concentrations of dustiness. This well correlated with the total dustiness amount. The occurrence of the Cu and Zn come from the exhaust of pyrometallurgical factories in the valley of the river Hornad north-westly from Košice. These factories have campaign production character and therefore the amount of dust is very variable and its correlation with the total dust is also low. The amount of Cr and the other trace elements is maximal about one order lower as the amount of subsidiary elements. This element and the other trace elements created not typical and inconstant trace element background. The positions of the Pb in the dust are in the residential agglomerations very specific. The amount of this element shows low correlation and zero regression. This phenomenon is caused by the fact that its genesis is footed not in the general dustiness but primarily in the amount of Pb containing additives in the exhaust of motor engines.

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