Environmental Characteristics of the Atmosphere of Residential Agglomerations* II**. Main, Minor, and Trace Elements in the Gravitation Dust Sediments

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It is necessary to observe the dustiness of residential agglomerations with respect to the chemical character of the gravitation dust sediments (precipitates), which secondarily influence also the chemical character of the airborne dust. The chemical character of the general dustiness was studied on the samples from four localities of the residential agglomeration of Košice on the N-S axis. This axis is recently the most frequent direction of prevailing winds (*ca.* 94 %) of the Košice basin. The influence of the geography of Košice basin on the total dustiness and also the chemical composition of the gravitation dust sediments were thus also observed. The Košice basin has a funnel-shaped character opening in the south direction. The elements of sediments were analyzed by atomic spectrochemical methods. The results of the monthly-collected samples were evaluated in differential histograms. With the selection and analysis of the chosen typical elements of the gravitation dust sediments, namely the main element Fe, the minor element Ti, and the cluster of trace elements As, Pb, Cu, Yn, Sr, Rb, and Zr, characteristic input data matrixes were acquired. These describe the situation not only in the Košice basin in Slovakia, but also in four typically different residential agglomerations in the GFR. The evaluation of the results of sampling of the sedimentary particles and the chemical determinations of the given elements enable to evaluate the element variability and the level of the toxicity of the studied residential agglomerations.

The observation of the chemical composition of main, minor, and trace elements of the gravitation dust sediments is necessary because these components contaminate the open soils as well as the whole area of residential agglomerations. The common main and minor elements (C, Ca, Fe, Mg, Mn, Si, and Ti) are present in gravitation dust sediments, except for C, which is present as graphite or pseudoamorphous carbon, mostly in oxidic compounds. On the contrary, some of the trace heavy metallic elements have the sulfidic (Bi, Cd, Co, Ni) or the sulfate (Ba, Sr, Pb) bond. The remaining metallic trace elements have the oxidic chemical form. This fact expressively complicates the development of analytical method of the excitation of powder samples because it induces undesirable matrix effect [1], which needs to be eliminated because it causes systematically wrong analytical results. It is necessary to divide the metallic trace elements into the following groups: the group of undoubtedly toxic elements (As, Be, Cd, Hg, Pb, and Tl), the concentration-conditioned toxic or essential elements (Al, Ba, Bi, Cr, In, Mo, Sb, Se, Sn, Sr, Te, W, and Zn), the exclusive essential elements (Cs, K, Li, Na, and Rb), and finally the indifferent elements (*e.g.* Hf, Zr).

EXPERIMENTAL

The method of the sampling of gravitation dust sediments used is defined in the norm VDI [2]. The sampling localities are identical with the localities given in Ref. [3]. The methods of the excitation of atomic spectra in the DC-arc [4, 5] as well as the method of excitation of atomic spectra in the dou-

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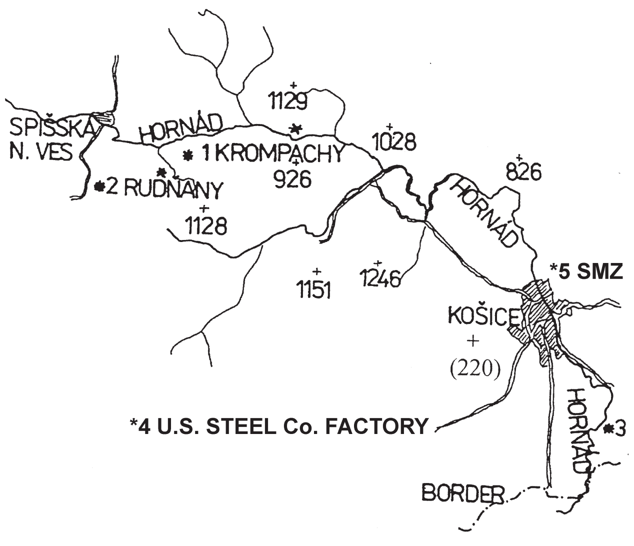

Fig. 1. Position of the pyrometallurgical factories in the Hornád river basin: *1 KROMPACHY – production of Cu; *2 RUDŇANY – production of Fe_2O_3 bailings; and the factories around the city Košice: *3 Incineratoring factory, *4 U.S. Steel Co. factory, *5 SMZ – Magnesite factory.

ble DC-arc [6] were used for the direct analysis of the powder samples. Finally, the energy-depressive fluorescence spectrometric method [7] was used for the result control. The efficiency parameters of these methods are discussed and evaluated in Ref. [8]. The results of all spectrochemical analyses (Table 1) of the powder samples were elaborated in the form of differential histograms. The monthly content changes of individual analytical elements $\Delta w(\mathrm{X})_i$ and the arithmetical mean values $\overline{w}(\mathrm{X})$ are calculated as follows

$$\Delta w(\mathrm{X})_i = w(\mathrm{X})_i - \overline{w}(\mathrm{X}) \qquad (1)$$

$$\overline{w}(\mathrm{X}) = \frac{1}{2}\sum w(\mathrm{X})_i \qquad (2)$$

where i represents the separate monthly samplings results: $i = 1,\ldots,12$.

The monthly analysis results $w(\mathrm{X})_i$ of the determined elements and the monthly amounts m_i of the sampled gravitation dust sediments are in Table 1. In this case, from the cluster of main elements of gravitation dust sediments only Fe was determined because its occurrence in the given content range is the most important from the environmental aspects. This element occurs [9] in the samples mostly in the oxide form (Fe_2O_3), and partially in the hydroxide form ($Fe(OH)_3$). On the surface of these compounds, the particles with the radius smaller than 10 μm containing toxic elements are adsorbed. Therefore, the toxicity of the Fe particles is rising [10]. From the cluster of minor elements, only the element Ti was determined. Recently, Ti is the most frequented minor

INPUT DATA MATRIX

i	Content values			m
1	$(c(\mathrm{X})_1)_1$	$(c(\mathrm{X})_1)_j$	$(c(\mathrm{X})_1)_Q$	m_1
2—11	$(c(\mathrm{X})_i)_1$	$(c(\mathrm{X})_i)_j$	$(c(\mathrm{X})_i)_Q$	m_i
12	$(c(\mathrm{X})_{12})_1$	$(c(\mathrm{X})_{12})_j$	$(c(\mathrm{X})_{12})_Q$	m_{12}
				$\sum m$

$\sum m$ – total dustiness/month; $j \in \langle 1, Q\rangle$; $i \in \langle 1, 12\rangle$.

Fig. 2. Matrix of the analytical value input data.

element of the atmospheric dustiness. In the given content range Ti is an essential element. Its average content level and its monthly fluctuation are conditioned mainly by the agricultural activity of the surroundings of Košice basin. From the group of toxic trace elements, As and Pb were determined because their occurrence in the atmosphere and in the gravitation dust sediments is frequent due to the anthropogenic and industrial activity. The elements Cu and Zn are present in the gravitation dust sediments in Košice basin due to the emissions of the near pyrometallurgical factories *ca.* 30 to 45 km north of Košice (Fig. 1). The selection of determined elements includes also Sr and Rb, because their toxicity is minimal and it is certainly possible to declare them together with Zr essential or at least environmentally indifferent elements [9, 10]. The changes of the content of these elements especially for the N-S direction of Košice basin were compared. Finally, the arithmetical mean values for the Košice basin were compared with the corresponding values of the GFR cities (Table 2): Mainz, Göttingen, Dortmund, and Jülich. For the chemometrical computations and evaluations of analytical results, individual input data matrixes were created for the detailed localities and year and monthly periods (Fig. 2).

DISCUSSION

The inquiry about the dustiness of the monitored region from the monthly amount of gravitation dust sediments m_i and the content data $w(\mathrm{X})_i$ of the determined elements was omitted. The predicted input data on the gravitation dust sediments amount changes, and the monthly change of the Fe main, Ti minor, and the cluster of trace elements content were used for the chemometrical evaluations.

The average values of the gravitation dust sediments amount (Table 1) for the individual localities of Košice basin confirmed that the geographical site and hereby modelled wind conditions formed the dustiness in the longitudinal N-S direction. The maximum dustiness is to be found in the localities Košice-centre (K-C) and Šebastovce (Š). As a consequence of expressive widening of funnel-shaped city basin, the wind speed decreases remarkably here. Therefore, the sedimentation of dust particles larger than with the diameter

Table 1. Arithmetical Means of the Amounts ($m/(\mathrm{g\ m^{-2}\ month^{-1}})$) of Gravitation Dust Sediments and the Contents of Main (Fe), Minor (Ti) ($(\bar{w}(\mathrm{X}) \pm s(w)_\mathrm{X})/\%$), and Trace Elements ($(\bar{w}(\mathrm{X}) \pm s(w)_\mathrm{X})/\mathrm{ppm}$)

Element	Locality			
	B	K-C	Š	H
		1st year		
Dust sediment	8 ± 3	15 ± 5	13 ± 5	5 ± 1
Fe	5 ± 1	5 ± 2	7 ± 3	4 ± 1
Ti	0.3 ± 0.1	0.3 ± 0.1	0.5 ± 0.2	0.4 ± 0.2
As	114 ± 33	183 ± 50	91 ± 30	84 ± 31
Pb	536 ± 155	350 ± 81	306 ± 42	428 ± 109
Cu	276 ± 53	177 ± 47	181 ± 31	235 ± 56
Zn	1587 ± 378	1040 ± 288	931 ± 315	1459 ± 676
Rb	98 ± 21	68 ± 19	94 ± 23	94 ± 13
Sr	143 ± 41	118 ± 34	152 ± 21	171 ± 24
Zr	145 ± 35	94 ± 26	127 ± 27	156 ± 50
		2nd year		
Dust sediment	5 ± 2	10 ± 1	11 ± 2	8 ± 6
Fe	4 ± 1	5 ± 1	6 ± 2	3 ± 1
Ti	0.4 ± 0.1	0.3 ± 0.1	0.2 ± 0.06	0.4 ± 0.1
As	147 ± 39	184 ± 61	100 ± 27	100 ± 64
Pb	508 ± 201	449 ± 69	339 ± 111	445 ± 401
Cu	325 ± 83	239 ± 43	220 ± 43	198 ± 100
Zn	1649 ± 491	1405 ± 211	1019 ± 258	1624 ± 892
Rb	74 ± 13	71 ± 9	78 ± 9	100 ± 20
Sr	128 ± 36	116 ± 19	127 ± 22	139 ± 37
Zr	109 ± 28	127 ± 16	109 ± 21	225 ± 96

10 μm increases. On the other hand, in the opening of Košice basin in the locality Bankov (B), which is 7 km north of the Košice-centre, the wind speed is the highest and therefore the amount of dust sediment is smaller. In the locality Hraničná (H), which is situated *ca.* 20 km south of the centre of Košice basin, the N-winds are markedly depleted of the dust particles. The S-winds, the frequency of which is only *ca.* 35 %, bring expressively less dust particles, because on the S-side of Košice basin there are less factories producing inorganic pollutants. Therefore, the total amount of gravitation dust sediments is in these localities lower. This phenomenon was confirmed for both the examined year periods.

The evaluation of the change of Fe main element and Ti minor element and also the cluster of trace elements of the gravitation dust sediments shows a remarkable phenomenon. The content value of the sediments for the months with considerable atmospheric precipitations shows also the highest amount of inorganic pollutants. This phenomenon is observed regardless of the total content of dustfall as well as the toxic, concentration-conditioned toxic, or essential or ecologically indifferent elements.

The differences $\Delta c(\mathrm{X})_i$ were calculated from the monthly values of the contents $w(\mathrm{X})_i$ of determined elements using eqn (*1*) and these values were used for the construction of differential histograms which illustrate the monthly variability $\Delta w(\mathrm{X})_i = f(\mathrm{month}_i)$. Extreme values also occur among the values of the histograms, which by their character exceed the leverage values, and it was therefore necessary to consider them for outliers. These extreme values were excluded from the original data matrix. Their position is conventionally marked with the symbol **D**. The criterion (*3*) of the exclusion was created on the basis of 3σ-criterion.

$$\Delta w(\mathrm{X})_i > \overline{w}(\mathrm{X}) + 3s(w_\mathrm{X}) \qquad (3)$$

The genesis of the determined elements in the gravitation dust sediments is specific with regard to the given residential agglomeration and its environment. The chemical composition of the sediment is on the one hand determined by the complex meteorological factors (wind speed, wind direction) and on the other one by the geographical site that regulates the transport of the polluted aerosol. The rain periods not only wash the aerosols but also generate different chemical reactions in the aerosols [10], mainly with aqueous character [11]. If the atmospheric precipitation has strongly acid character, it is necessary to calculate with the formation of difficultly soluble sulfates (*e.g.* $PbSO_4$, $SrSO_4$).

The element Fe (Fig. 3) is besides C, Ca, Mg, and Si the main and significant pollutant of the gravitation dust sediments and causes most environmental complications. In the Košice basin Fe enters the atmosphere mainly by industrial emissions. Except the U.S. Steel Co. it is the incinerating factory of residential waste in Kokšov-Bakša, 7 km south of Košice-centre, and the pyrometallurgical factories *ca.* 30 to

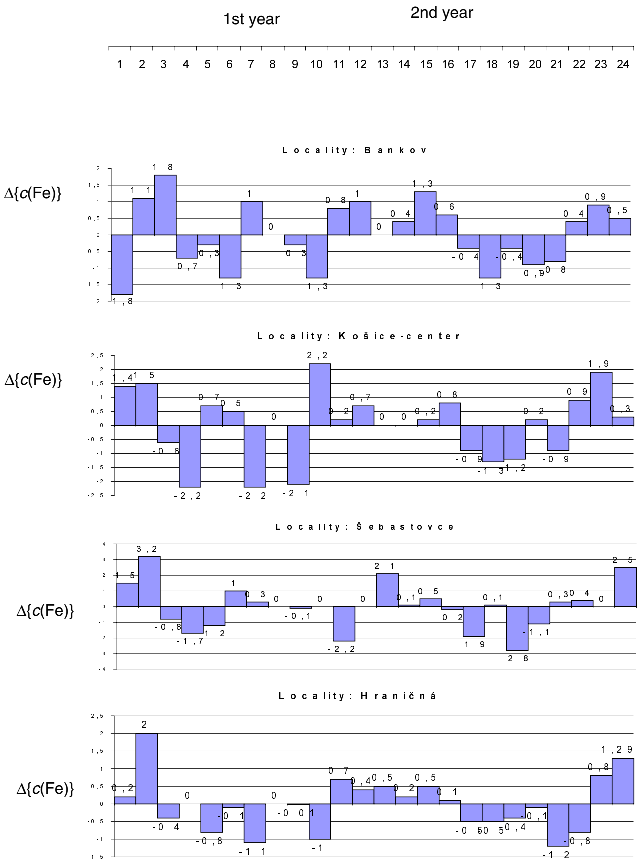

Fig. 3. Differential histograms of the monthly change of Fe content.

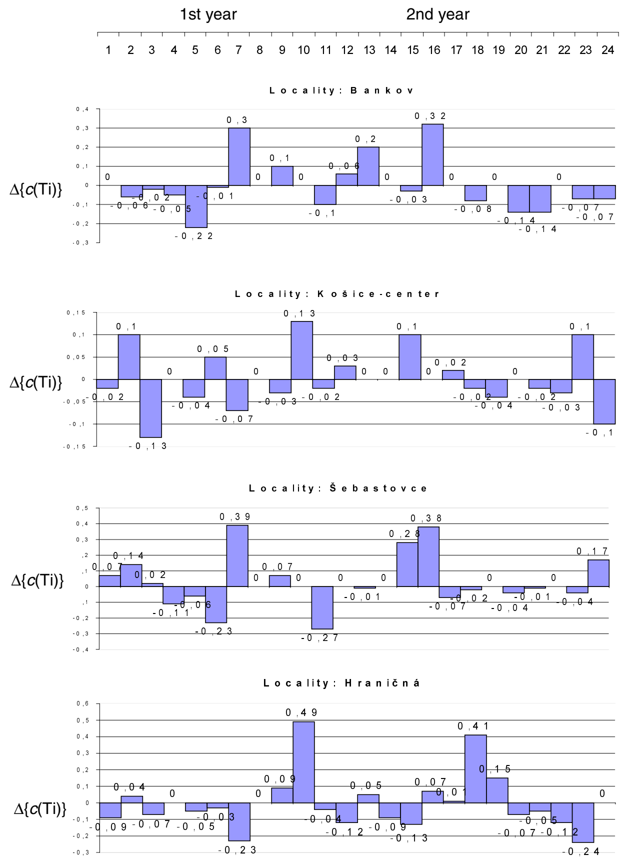

Fig. 4. Differential histograms of the monthly change of Ti content.

45 km north of Košice-centre the exhalations of which are brought by the northern winds. The concentration of Fe in the given sediment is mainly influenced by the campaign parameters of the factories given above, and only secondarily with the meteorological factors, which are the amount of the atmospheric precipitation and the prevailing winds. The periodical monthly changes of the Fe content in the individual localities of the Košice basin are characterized by the systematical reducing of the value $\Delta w(\mathrm{X})_i$ in the summer months. In this period, the monthly atmospheric moisture is lower than in winter and partially also than in the spring and autumn months. The total variance of $\Delta w(\mathrm{X})_i$ values of both the compared year periods is similar, which is conditioned by the constant prevailing N- and S-winds, which follow the axis of funnel-shaped Košice basin. It is remarkable that the change of the content of individual trace elements, and also the change of Fe content do not follow the total change of the amount of gravitation dust sediments. The locality Bankov *ca.* 8 km north of the Košice-centre is the least contaminated by the industrial activity. However, the all-year variance of the Fe content in the locality Košice-centre is very expressive. This occurs from March until October and is caused by the change of N- and S-winds. It is the N-winds that cleanse the Košice basin from the pollutants of the incinerating factory and partially also from the trade units of the U.S. Steel Co., west of the Košice-centre.

Also remarkable is the variance of the Ti minor element (Fig. 4), which does not originate in the industrial activity but in the primary agricultural cultivation activity. In the localities Bankov, Šebastovce, and Hraničná there are numerous maxima and minima visible on the differential histograms, which from the statistical point of view are not possible to be considered for outliers but only for leverages. This occurs in the months, when by the synergistic effect the meteorological influences (rain, snow, fog) and the prevailing N- and S-winds are added to the intensive agricultural activities (ploughing). These statements also confirm the fact that in the locality Košice-centre, which is the least contaminated by the agricultural activity, the variability of Ti is minimal. From the ecological point of view, Ti behaves as an element with the background character. The rise of Fe, and partially Ti content, negatively influence the global toxic character of the gravitation dust sediments and thus the toxicity of the atmosphere of the observed region. In the periods when the $\Delta w(\mathrm{Fe})_i$ and $\Delta w(\mathrm{Ti})_i$ values are positive, the amount of adsorbed trace elements on the surface of Fe and Ti compounds of the sediments rises.

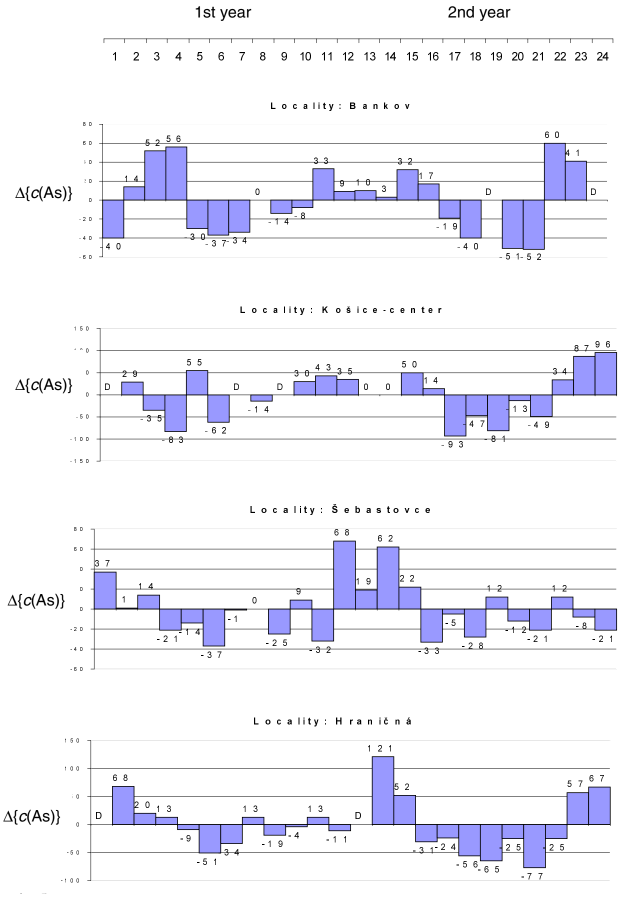

Fig. 5. Differential histograms of the monthly change of As content.

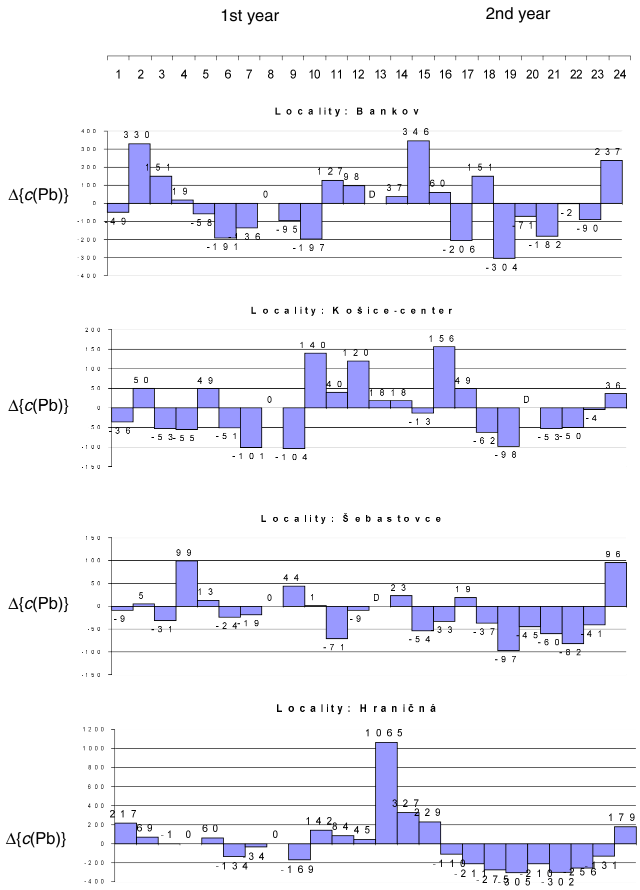

Fig. 6. Differential histograms of the monthly change of Pb content.

For the given residential agglomerations, the elements As and Pb were the most actual from the cluster of toxic elements. As enters the atmosphere and thus the gravitation dust sediment mainly by the products of incineration of fossil fuels, and by the pyrometallurgical activities, the materials of which contain the mineral arsenopyrite in trace amounts. In the given region there are only the small-consumers of fossil fuels (brown coal). Their part of the total amount of burned fuels in the period of heating is *ca.* 30 to 45 %. At the same time As presents the highest monthly variability (Fig. 5) and the most excluded extreme values $\Delta w(\mathrm{As})_i$. In the northern part of Košice basin and in the Košice-centre, in both the years from April to September an expressive minimum of the As concentration occurs and the variability of $\Delta w(\mathrm{As})_i$ values is very high as well. In the localities in the southern part of the tested residential agglomeration (Šebastovce, Hraničná), the total amount of gravitation dust sediments and also the As concentration are very low. Similarly the variability of As in this locality is lower.

The average content of Pb (Fig. 6) in both the year periods is remarkably higher than the content of As (Table 1). The decrease of the Pb content from April to October is significant. The variability of Pb content in the locality Košice-centre is the highest, because the fluctuation of the automobile traffic is the highest in this locality. This traffic using fuels with Pb antidetonator additives generates a high level of toxicity of the atmosphere and the gravitation dust sediments. The best balanced is the Pb variability in the locality Šebastovce, because here the uninterrupted automobile traffic is dominant. In the locality Hraničná this variability rises, because in this area the influence on the dustiness creation and on the Pb content is determined by the badly interpretable accidental factors resulting from the specific regime of the border control area.

As the conditioned toxic elements it is necessary to regard those elements, which under the defined element specific level ($w(\mathrm{X}) \approx 1000$ ppm) are essential, but well over this level acquire toxic character [9, 10]. In the examined region northwest of Košice basin (Fig. 2) in the river basin of Hornád there are the pyrometallurgical factories (Krompachy, Rudňany), which contaminate the atmosphere besides Fe and As also with the content of conditioned toxic elements Cu (Fig. 7) and Zn (Fig. 8). This contamination has an expressive campaign and seasonal character. The N- and NE-winds, the frequency of which is in the Košice

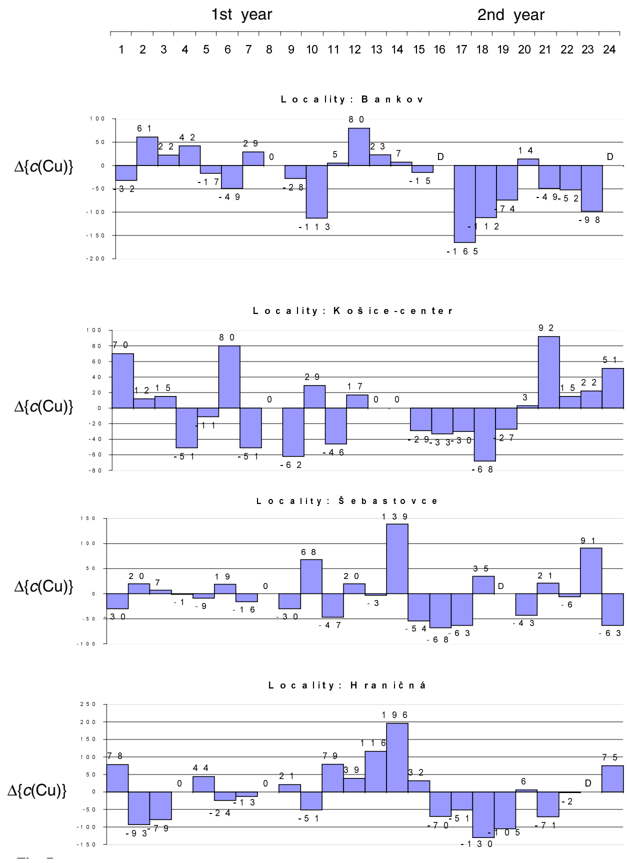

Fig. 7. Differential histograms of the monthly change of Cu content.

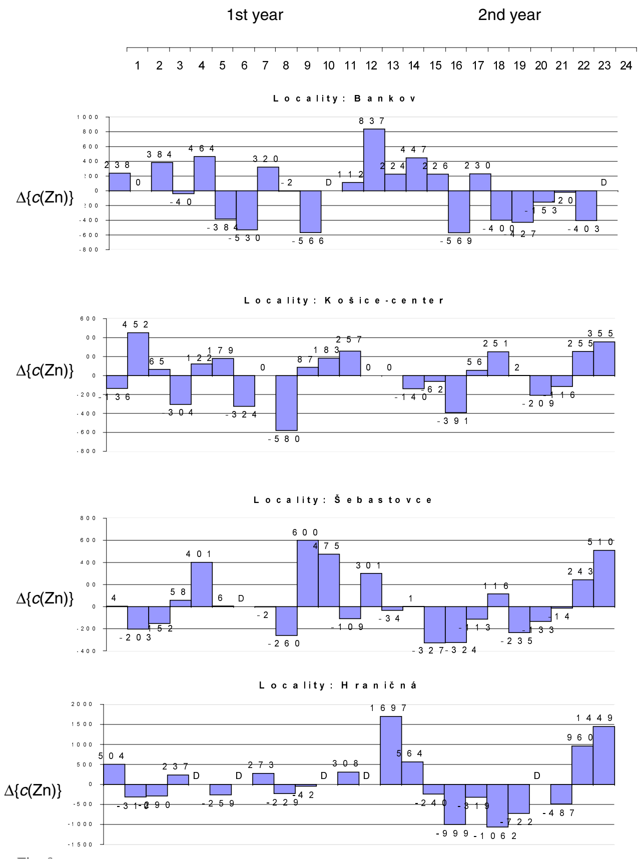

Fig. 8. Differential histograms of the monthly change of Zn content.

basin *ca.* 60 % bring the emissions from the area of pyrometallurgical factories, which then sediment in all parts of the Košice residential agglomeration. The irregular campaign character of the contamination of atmosphere with the pollutants is more expressively demonstrated in the locality Bankov, especially in the second year period. In the locality Košice-centre, the Cu content in the gravitation dust sediments is the best balanced (Table 1), which is confirmed also by the low values of standard deviations $s(w_{\mathrm{Cu}})_i$. In the localities Košice-centre and partially also Šebastovce the variability of $\Delta w(\mathrm{Zn})_i$ is generally low and from April to October it is the lowest. This means that in the given dry period the atmosphere is the least washed by the atmospheric precipitates, mainly by the rains. Very extreme values $\Delta w(\mathrm{Zn})_i$ are reached in the second year period in the locality Hraničná. The extremely high values in the months February, November, December, and the extremely low values in the months May, July, and August were caused by the extremely high and extremely low atmospheric precipitation in the given months.

The elements Sr (Fig. 9) and Rb (Fig. 10) in the content value under 1000 ppm, until Sr does not show remarkable radioactivity, are from the chemoecological aspects considered as essential elements. Their occurrence in the atmosphere of the studied residential agglomerations has a background character and is not induced by industrial activities. The validity of this is also confirmed by the inexpressive fluctuation of their concentrations (Table 1). The monthly changes of their content are shown in the differential histogram. The rule that in the dry months the gravitation dust sediments are demonstrated by negative $\Delta w(\mathrm{X})_i$ values was confirmed. In the locality Šebastovce, which is situated on the southern end of Košice basin, the variability of $\Delta w(\mathrm{Sr})_i$ and $\Delta w(\mathrm{Rb})_i$ values is the lowest. From the chemoecological aspects until reaching the content-limiting value *ca.* 1000 ppm the element Sr is wholly indifferent, or indefinitely essential element. Their occurrences in the atmosphere regularly have only a background character [10].

The rise of the Zr content over 500-ppm level refers to the presence of industrial contamination. Such pollutants can come from the systematical incineration of the unsorted residential waste containing glass and ceramic materials. The rises of the average Zr content in the locality Hraničná confirm this, because between the localities Šebastovce and Hraničná the incineratoring factory of the unsorted residential waste is found. The campaign character of the activity of this factory is shown also on the observed changes of differential

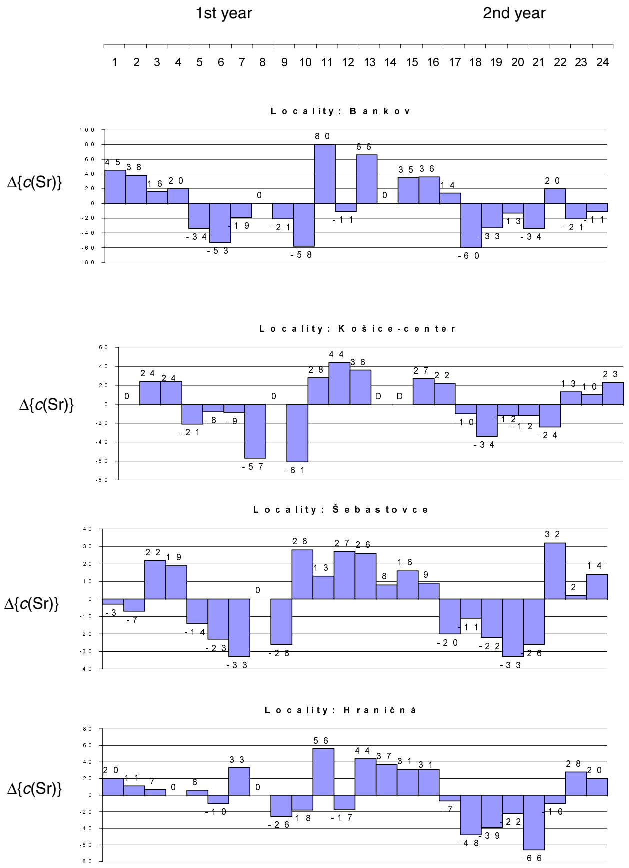

Fig. 9. Differential histograms of the monthly change of Sr content.

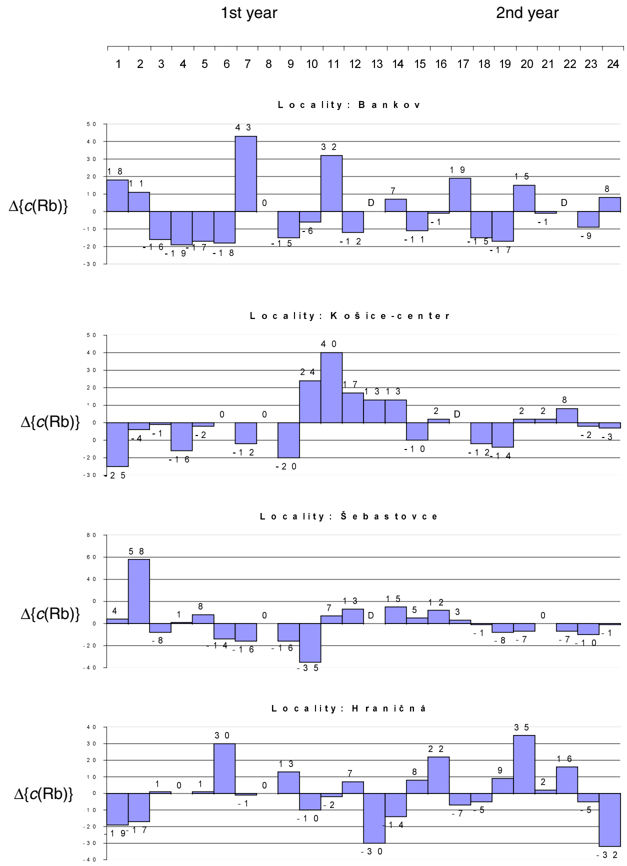

Fig. 10. Differential histograms of the monthly change of Rb content.

histograms (Fig. 11) mainly in the second year period.

The comparison of the chemical character of the dustiness of residential agglomeration of Košice basin with four residential agglomerations in the GFR (Table 2) confirmed the statement [12] that the German residential agglomerations are marked with lower dustiness. The level of the content of trace elements in the gravitation dust sediments is also lower, only the Cu content is equal in all the compared German localities. Therefore it is possible to consider Cu in Germany a background element. That is for such industrially high-developed West-European country wholly well founded. The most remarkable differences are observed at comparing the contents of toxic elements As and Pb. The low level of As in Germany may be assigned to an expressively lower consumption of fossil fuels by the small-consumers and the effective dust separation of the gaseous products of the incinerator

Table 2. Arithmetical Means of the Contents of Main (Fe), Minor (Ti) $((\bar{w}(\mathrm{X}) \pm s(w)_{\mathrm{X}})/\%)$, and Trace Elements $((\bar{w}(\mathrm{X}) \pm s(w)_{\mathrm{X}})/\mathrm{ppm})$ in Gravitation Dust Sediments

Element	Locality				
	Mainz	Göttingen	Dortmund	Jülich	Košice
Fe	2.8 ± 0.9	3.0 ± 1.0	10.9 ± 2.0	5.3 ± 2.1	15.2 ± 5.0
Ti	0.22 ± 0.04	0.30 ± 0.02	0.32 ± 0.20	0.31 ± 0.10	0.21 ± 0.02
As	14.5 ± 1.0	7.5 ± 0.6	19.2 ± 1.2	25.0 ± 3.5	183.0 ± 50.0
Pb	3.5 ± 1.0	2.2 ± 0.7	2.4 ± 0.7	3.6 ± 1.5	350.0 ± 81.0
Cu	84.0 ± 1.2	96.0 ± 2.0	168.0 ± 2.3	102.5 ± 5.0	177.5 ± 47.0
Zn	37.0 ± 2.5	35.0 ± 2.0	48.0 ± 2.9	50.5 ± 4.2	1040 ± 288
Sr	16.0 ± 2.5	9.5 ± 0.7	12.0 ± 0.3	30.0 ± 5.0	68.0 ± 19.0
Rb	27.0 ± 4.0	20.5 ± 7.5	11.5 ± 0.7	30.0 ± 5.0	118 ± 34.0
Zr	40.5 ± 12.5	18.0 ± 2.1	12.5 ± 0.6	20.0 ± 0.7	94.0 ± 26.3

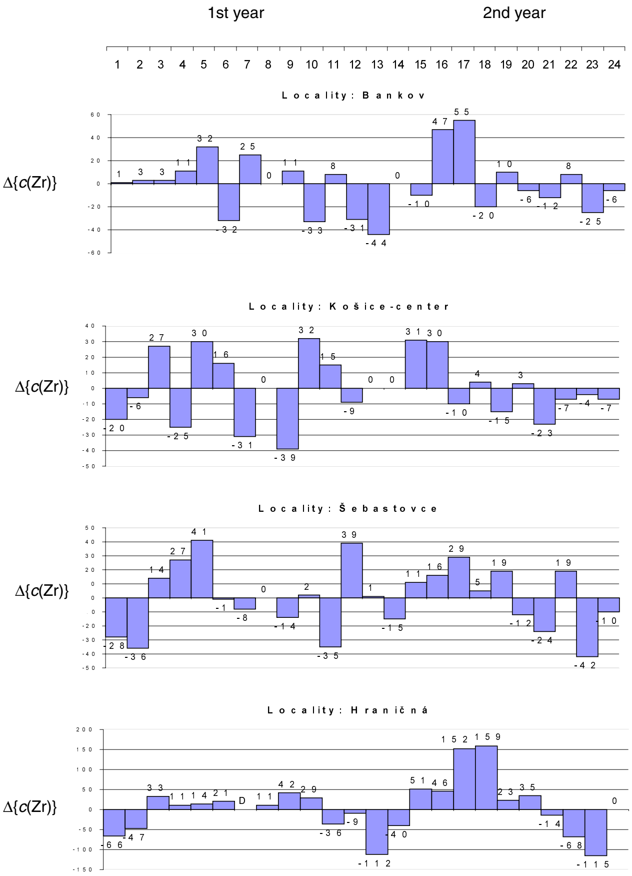

Fig. 11. Differential histograms of the monthly change of Zr content.

aggregates. The lower level of Pb in the German atmosphere is given by the fact that in the West-European states the ratio of automobiles with catalytically additional burning is remarkably higher than in Slovakia. The toxicity of the atmosphere in Germany is therefore remarkably lower than in Slovakia. This circumstance is caused by the fact that the Slovak industrial dust- and soot-collecting aggregates operate with lower efficiency than those in the West-European factories.

The mean monthly values of essential elements Sr, Rb, and Zr are lower in Germany and have a background character. Their monthly variation is systematically the lowest in the centre of the residential agglomeration of Košice.

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