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Heavy Metals in Sedimentary Dust in the Industrial City of Lukavac

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Abstract

Environmental pollution caused by sedimentary dust (SD) and heavy metals (HM) is a problem for many years in the Lukavac, Bosnia and Herzegovina. The main aim of this paper is to perform monitoring of air pollution in the area of the city by measuring of sedimentary dust emissions, different metals associated with it, and probable adverse effects on human health. The samples of SD were collected monthly from six locations in industrial and urban parts of city. Metal concentrations in total SD were determined by using Perkin-Elmer model Inductively Coupled Plasma and statistically evaluated with SPSS 17.0 statistical program. The quality of ambient air is discussed along with the meteorological conditions. The results presented indicate that the meteorological parameters, wind speed and direction, were significant factors for SD distribution. There was a correlation between some metals (K, Sr, Mn, Cr, Cu and Co) and SD distribution. The daily limit values for contents of SD proposed by national "Regulations on air quality"(350 mg/m^2d) exceed at two measuring points. The average maximum content of SD was 993.57 mg/m^2d, downwind of cement and soda factories, and the average minimum was 215.78 mg/m^2d at EP gas pump. Concentrations of ecotoxic metals, Pb, Cd and Zn in SD, usually exceed proposed limit values. Concentrations of pollutants hazardous to the environment as Ni, Co, Cu, Cr, Mn and V, vary from one site to another. Activities in industrial plants are responsible for the highest percentage of emissions in the air, with possible health impact on the surrounding population. The other sources of pollution are automobile traffic and individual furnaces.

Keywords: Air pollution, sedimentary dust, heavy metal, environment, cement dust

1. Introduction

The air pollution in Lukavac, the industry and mining region of Bosnia Herzegovina, (140 km north of the capital Sarajevo, 14 km west of Tuzla), is perceived as the main environmental problem in several last decades. In industrial zone near urban area of Lukavac are closely placed chemical industries: Cement Factory in Lukavac (FCL) and Soda Factory in Lukavac (SSL, about 300 m northwest from FCL) and Global Ispat Coke Industry d.o.o Lukavac (GIKIL) with plant for nitrogen fertilizer, placed about 3 km in the same direction. Urban area is located in the east part of the municipality and it has a total population of 57000. Lukavac is bordered by the area of forest, agriculture parcels and Municipality of Tuzla from southeast; on the east side it is surrounded by pit and coal waste Šićki Brod. On the north it is also surrounded by building land and pit. On the north-west is Puracic and on the south-west and south is surrounded by agricultural land and with one part of it enters in an industrial zone. In the municipality of Lukavac you can also find lignite pit called Sikulje (cca 4 km) as well as limestone quarry called Vijenac (cca 11 km). Both Tuzla and Lukavac are established along the banks of the Spreca River, a tributary of the Bosnia River which flows into Sava and the Danube, an international waterway.

Gaseous emissions of pollutants and dust particles are created from industry, but also individual furnaces and automobile traffic. Daily monitoring of air pollution is being conducted in the city, but without heavy metal contents in sedimentary dust analysis. Recently, in the city you could often hear accusations that the dust particles emitted from different sources contain adsorbed heavy metals, which cause frequent occurrence of respiratory disease in the city population. Also, sedimentary dust has the primary effect on soil pollution, especially if heavy metals and various organic compounds are adsorbed on its surface. The total sedimentary dust presents all substances in solid, liquid and gaseous state that are not part of the air, and deposit itself by the gravity or rinsing rainfalls from the atmosphere to the ground. Large particles are primary measure of visible pollution of the environment, since they are deposited on all surfaces in the human environment. Depending on the chemical composition of particles of sedimentary dust, quantity and type of adsorbed compounds, the impact of this type of dust may be more or less harmful. Sedimentary dust, except that impairs the quality of air, reaches and pollutes water and soil and thus indirectly leads to the endangerment of the environment. It also falls onto the leaves of the plants which make them close their pores called stomata, it affects the growth of the plant and it damages it. The existence of moisture in the atmosphere causes the particle spread partially and get into the plant through epithelia. The metals accumulate in the soils from polluted air. Soil contamination by heavy metals such as Pb, Cr, Cu, Mn, Ni, Zn and Cd is a matter of great concern. Unlike organic contaminants that loose toxicity by the time with biodegradation, heavy metals cannot be degraded, their concentration can be increased by bioaccumulation and they have toxic effects at low concentrations (Aksoy, 2008). Although low quantities of some heavy metals, such as copper and zinc, are essential for many organisms, they are potentially toxic and accumulate in soil over long period of time and this result in soil pollution (Ahmad et al, 2008). Over a period of time different sources enrich heavy metals in soil. Excessive heavy metal contents changes the soil quality which affects the normal use of soil or endangering public health and living environment. Pollution of agricultural soils by heavy metals may lead to reduced yields and elevated levels of these elements in agricultural products and thus provide their entrance into food chain. Soil constituents may immobilize heavy metals, so prevent or reduce the detrimental effects on soil organisms, crops and ground water quality (Blume and Brummer, 1991).

This study was carried out in order to determine the effect of these suspicions, establishing SD immission in the city area and heavy metal determination in it.

Sisecam soda Lukavac (SSL) d.d. is a chemical manufacturing company which produces soda ash using the Solvay process. The plant currently produces light soda ash and refined sodium bicarbonate, pigments and inorganic dyes. The capacity of the plant is 250000 tons per annum. All raw materials, except ammoniac, are available within a 20 km radius around the plant. Coal comes from an underground mine, limestone is supplied from a quarry Limestone Mine called Vijenac, 17 km south of Lukavac and brine is pumped in salt mines located 23 km away under the city of Tuzla. The plant is disposing solid waste inside the plant (carbonate and black sea) and outside the plant (white seas covering an area of 56 ha). In SSL about 900 tons of coal is burnt per day as fuel. Control system for the plant is not completely effective. Cement factory of Lukavac (FCL) produce clinker and cement as an important binding agent for construction industry. The preparation of cement involves mining; crushing and grinding of raw materials; calcining the materials in a rotary kiln, cooling the resulting clinker, mixing the clinker with gypsum; and milling, storing and bagging the finished cement. The process generates a variety of wastes, including dust and gases. A central process step during the manufacturing of cement is the production of the intermediate product clinker. For this production, inorganic raw materials are burnt at temperatures in the range of 1500°C. Regular fuels are coals, oil or gas. Natural fuels or raw materials may contain trace metal elements which may be either transferred into product cement clinker, cement kiln dust (CKD) or emitted with the exhaust gas into the environment. Dust emissions from cement plants can be controlled by using de-dusting equipment in the form of filters or electrostatic precipitators (Huong, 1996). As raw materials, FCL use limestone supplied from a Limestone Quarry Vijenac, fly ash and slag from Power Plant Tuzla and quartz sand. In FCL 250 tons of coal is burnt per day as fuel. A capacity of FCL is 840000 tons of cement per annum and there is effective control system for the plant.

In this paper, by comparison of the environment situation in the vicinity of cement and soda plants in Lukavac, we attempt to emphasize the air quality in the surroundings of these plants. The scope of this paper is to provide the results of measurements of the total deposition dust and those elements that are characteristic of industrial production activities or are particularly ecotoxic: K, Ba, Sr, Mn, Zn, Cd, Ni, Pb, Hg, Cr, Co, Cu, As and V. Measuring of sedimentary dust concentration was performed using the Bergerhoff method (VDI 2119, sheet 2., 1996). Although this method of measuring mean continuously measuring sedimentary dust throughout the year, when establishing the annual trend sedimentary dust concentration, the measurements were done for a period of four months, since they are intentionally aimed at proving the presence of heavy metals in sedimentary dust in region of Lukavac, which gives preliminary character. Fall period in samples of sedimentary dust collected during the summer and autumn was period of four months. The movement and fate of dust depends on the physical nature of the dust and meteorological conditions of the surrounding areas. Air quality for total sedimentary dust, Pb, Cd, Zn and Tl in the study area was evaluated by comparing the mean monthly values with limit values proposed by the Regulations on air quality (Official Gazette FBiH No.12/05). Total deposition dust is also compared with German standards (TA Luft standards, 1986).

2. Experimental

2.1. Chemicals, Reagents and Glassware

All chemicals and reagents were of analytical grade and were purchased from: (Himedia – India: PAN indicator, Kalcein, Methyl thymol blue, Bromophenol blue, methyl orange), (Riedel de Haën: Barium chloride), (Merck – Alkaloid: Manganese(II) sulfate tetrahydrate), (Lachema – Czech Republic: acetic acid, ammonia), (Semikem – Sarajevo: triethanolamin, potassium hydroxide, hydrogen peroxide, phosphorous acid, sulfuric acid, potassium permanganate), (Zorka – Šabac: sulfosalicil acid, komplexon III, ammonium nitrate, ammonium chloride), (Penta: sodium carbonate, potassium carbonate, chloric acid, nitric acid), (Kemika – Zagreb: ammonium acetate, ammonium thiosulfate, stannous chloride dihydrat, mercury (II) chloride, ammonium oxalate, ammonium hydrogen phosphate, potassium dichromate, silver nitrate). All standards were prepared from reagent grade chemicals (Perkin Elmer Pure – Atomic Spectroscopy Standard). All glassware was rinsed successively with detergent and distilled water three times prior to use.

2.2. Sampling

Sedimentary dust samples were taken from 6 different stations in 4 months (20th July to 18th November 2009), and could not be taken from December to March because of the snow and climatic conditions. Coordinates were determined by Global Positioning System (GPS). Dust samplers, filled with 100 cm^3 of 10 % isopropyl alcohol, were used for the monitoring of sedimentary dust at all the locations at an approximate height of 1.5 m from ground level. The samples were continuously collected monthly for 4 months.

2.2.1. Determination of Sedimentary Dust Mass

Collected samples of sedimentary dust were washed up and vacuum-filtered through Whatman white filter-paper, dried in dry kiln at 105° C until they reached constant weight. The mass of collected dust was determined gravimetrically after drying. Dried samples were stored in polyethylene bags in desiccators to avoid contamination throughout the analyses.

2.2.2. Determination of Heavy Metals Concentration

Triplicate subsamples of approximately 1 g of well homogenized sediment samples were accurately weighed on an analytical balance and then burnt on filter papers and glowed in platinum or porcelain dishes at temperature of 1000° C to remove organic matters. After that, dust samples were transferred into glass digestion tubes and digested in concentrated chloric acid and diluted to a final volume of 500 cm^3 using double distilled water. The filtrate was examined for the concentration of metals: K, Ba, Sr, Zn, Pb, Mn, Ni, Cu, Cr, Co, Cd and V by *Inductively Coupled Plasma-Optical Emission Spectrometer*, ICP-OES OPTIMA 2100 DV, Perkin-Elmer, with the standard of 100 mg/dm^3 for metals. The results were expressed in mg/dm^3 of filtrate. Data presented are average of three replications.

2.2.3. Ambient Air Quality Monitoring

Meteorological data at the site were collected from the Meteorological Station Modrac (Public Water Service Company "Spreča" d.d.Tuzla) to provide correct temperature and wind data for the interpretation of results.

2.2.4. Statistical Analysis

All analysis was performed using the SPSS 17.0 statistical program. Data were statistically analyzed by one factor analysis of variance (ANOVA) followed by Tukey HSD post test for multiple comparison. Pearson correlation coefficient (r) was used to calculate the degree of linear association between different locations and to determine the relative association among metals and between metals and sedimentary dust. A two-tailed probability less than 0.05 ($p<0.05$) was considered to be significant.

3. Results and Discussion

3.1. Total Content of Sedimentary Dust

Limit values for total sedimentary matter and metal concentrations in it are defined by the directives of "Regulation on limit values of air quality" (Table 1). Limit values are those from which are not expected to have harmful effect on the environment but if exposured, there is the risk.

Table 1: Limit values of the air - for sedimentary dust

Pollution matter	Period of sampling	The average anual level (mg/m^{2}d)	High level (mg/m^{2}d)
Sedimentary dust - total	One month	200	350 *
Pb in sedimentary dust	One month	0,100	
Cd in sedimentary dust	One month	0,002	
Zn in sedimentary dust	One month	0,400	
Tl in sedimentary dust	One month	0,002	

* applies on the month in the year with the highest value of deposition/sediment

Six monitoring sites were selected. Distance between measuring points are about 800 - 1000 m. All the six locations are as: (1) Gas Pump EP- about 450 m away in south west side, (2) Gas Pump J. Kopex - about 850 m away in southeast, (3) Dzhenex supermarket - about 450 m away in northeast side, (4) central bus station Lukavac about 950 m away in northeast side, (5) Kulina bana street 9 - about 900 m away in northwest and (6) cemetery- about 850 m away in northwest side from factories. Topographically the monitoring locations are given in Figure 1 and Table 2. The Gas Pump EP and the Gas Pump J. Kopex are located next to the state road, whereas cemetery is near the SSL chemical plant. All the locations were also influenced by the vehicular pollution.

Table 2: Locations of measurements points for sedimentary dust

No	Measurement point	x-axis	Y-axis	Height
1	Gas pump EP	4 925 687,63	6 542 789,28	149,62
2	Gas pump J. Kopex	4 925 687,63	6 542 789,28	152,62
3	Dzhenex center	4 925 687,63	6 542 789,28	153,62
4	Bus station Lukavac	4 925 687,63	6 542 789,28	151,62
5	Kulina Bana street 9	4 925 670,98	6 542 792,02	147,62
6	Cemetery	4 925 670,98	6 542 792,02	144,62

Figure 1: Distribution of monitoring sites in the area of Lukavac city

Sedimentary dust concentrations and distributions at different monitoring sites are shown graphically in Figures 2 and 3.

Figure 2: Mean sedimentary dust concentrations (mg/m^2 d) at different locations of Lukavac

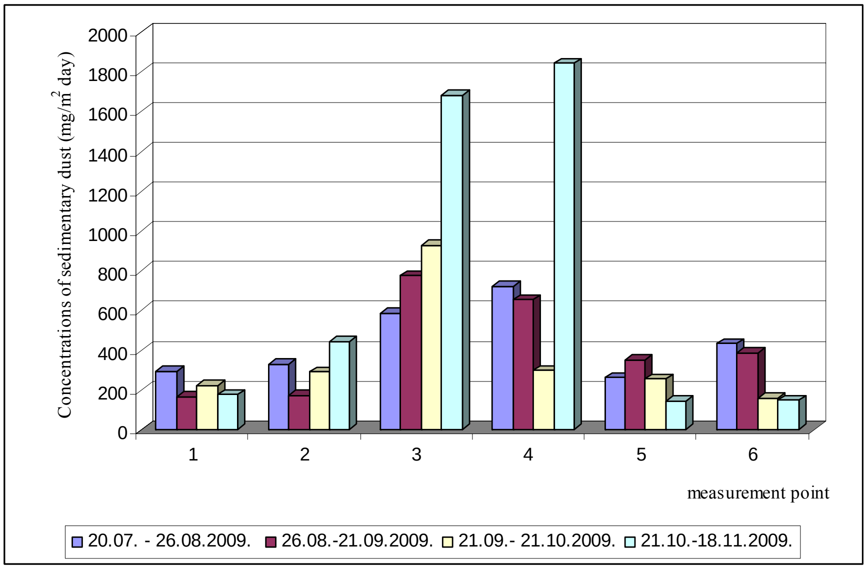
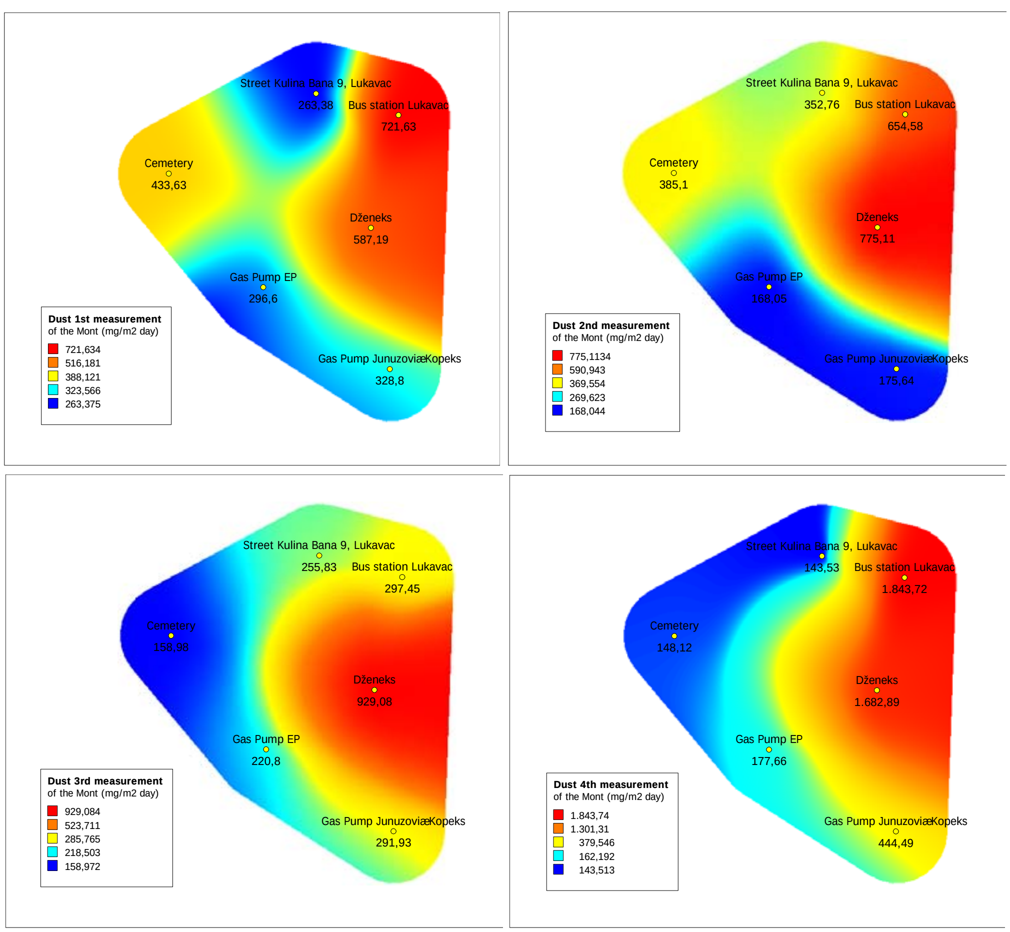


Figure 3: Distribution of sedimentary dust at different locations of Lukavac area during four months



During investigated period, the daily mean of average temperature in summer ranged between 22.2 °C (July/August) to 20.42 °C (August/September) and in autumn between 14.31 °C (September/October) to 8.98 °C (October/November). The prevailing wind direction being from the south (average velocity 1.05 m/s) and east (average velocity 1.20 m/s). Low or zero wind conditions occurred regularly more than 43 % of time. Calm conditions, light and variable winds are likely to cause very high localized concentrations of pollutants. In Fig. 2 it is obvious that the environment in the surrounding of industrial plants is strongly polluted. The average total depositions at all sampling sites were exceeded limit values.

Total mass of SD at all the locations have been arranged in descending order as:

3 > 4 >> 2 > 6 > 5 >1

Heterogeneous variations in the concentrations of trace metals prompted us to transform the data on sedimentary dust by using the $\log_{10}$ to make them homogenous. The transformed data are then submitted to statistical analysis such as analysis of variance (ANOVA) and correlation. Equality of mean differences in SD concentrations of different locations has been carried out by one-way analysis of variance (ANOVA) (Table 3). Significant ($p<0.05$) difference is observed between locations ($F = 6.623$).

Table 3: Analysis of variance summary – sedimentary dust

Source of variation	**Sum of Squares**	**df**	**Mean square**	**F**	**Sig.**
Between Groups	1.493	5	0.299	6.623	0.001
Within Groups	0.811	18	0.045		
Total	**2.304**	**23**			

A pair wise comparison between locations was done by Tukey post hoc test (Table 4) to know which pair differed in the mean level. Mean concentrations of sedimentary dust at Dzhenex center are significantly ($p<0.01$) higher and different from other locations, except the bus station, while mean sedimentary dust in rest of the locations are not significantly ($p>0.05$) different, *i.e.* nearly equal, except between bus station and gas pump EP.

Table 4: Comparison of sedimentary dust by Tukey test (DF = 18)

Comparisons		**Significance**
Dzhenex center	Gas pump EP	*
	Gas pump J. Kopex	*
	Bus station Lukavac	ns
	Kulina Bana street no. 9	*
	Cemetery	*
Bus station Lukavac	Gas pump EP	*
	Gas pump J. Kopex	ns
	Kulina Bana street no. 9	ns
	Cemetery	ns
Kulina Bana street no. 9	Gas pump EP	ns
	Gas pump J. Kopex	ns
	Cemetery	ns
Gas pump EP	Gas pump J. Kopex	ns
	Cemetery	ns
Gas pump J. Kopex	Cemetery	ns

ns = not significant ($p> 0.05$), * = significant ($p< 0.05$)

Fluctuations of monthly sedimentary dust mass concentrations can be observed. Mean sedimentary dust concentration at location 3, shopping center Dzhenex (993.57 mg/m^2d,) is found to be maximum, while the location 1, gas pump EP, registered the minimum (215.78 mg/m^2d). However, sedimentary dust concentrations were clearly higher at locations 3 and 4 compared to concentrations at locations 1, 2, 5 and 6. This suggests that distance is not the only factor to be taken into account when evaluating air quality for a particular area. The highest sedimentary dust concentrations at these locations were observed during November 2009, when the south wind prevailed, and the temperatures were low. In general, a high degree of monthly variability could be attributed to the role played by the meteorological variables in the valleys, as well as changes in industrial activity throughout the year. Lukavac is situated in valley bordered from the northeast with high hills. Atmospheric conditions in autumn and winter favor the accumulation of pollutants in the valleys, in a phenomenon known as air mass stagnation (Querol et al, 2008; Lertxundi at al, 2010). The prevailing wind in winter is predominantly from the South, which is opposite to the sampling sites 3 and 4, and in the summer months, from the South and East. This information suggests that the air masses tend to move down the valley, towards the town of Lukavac (especially in winter), thus impeding the upward flow of air. Cool air tends to flow downhill into the valley so aggravating the problem of low level inversions. Mixing between the air in the valley and the air above is reduced. The pollutants are then trapped between the inversion height and the ground (Harrison, 1997).

As per ambient air quality standards in Bosnia and Herzegovina, the annual average value for sedimentary dust is 200 mg/m^2d, while mean-year total deposition dust tolerance level is much higher, 350 mg/m^2d. Similar values are proposed by German standard. The average values of sedimentary dust at measuring points 3 and 4 are at least two or three times higher than limit values proposed by the both standards. Exceeding over monthly limit values of sedimentary dust concentrations at these locations (as shown in Figure 2), occurred probably due to high industrial activities in these periods. Daily production in SSL is about 700 tons of soda, where 1.25 tons of coal is used per soda tone. This means that SSL burns 900 tons of coal per day, producing about 175 tones of fly ash and slag as by-product of coal burning. From those 175 tons, 35 of it is slag, which means that there are 140 tons of fly ash. Today´s electrostatic precipitators in soda fabric are not totally reliable, they are obsolete and don´t work properly and don´t fulfill the requirements set by the current standards when it comes to the allowed level of mechanical waste. The consequences are those that hundreds of tons of fly ash fall directly into the city and Lukavac Municipality, which has a great impact on human health and ecosystem. Cement kiln dust is a very important by-product of cement industry. FCL produces 20-30 thousand tons of CKD per year. After the renovation, dust emissions from FCL are controlled by using de-dusting equipment in the form of baggy filters, so the most quantity of CKD is being returned back to the process. However, dust deposition could be caused by still continuing dust emissions (Tervahatty et al, 2001). Cement dust contains heavy metals like Ni, Co, Pb, Cr, pollutants hazardous to the biotic environment, with impact for vegetation, human and animal health and ecosystems (Kumar et al, 2008).

Measuring points 1 and 2 are located near station road outside of the city. At these stations, the mean sedimentary dust values varied from 215.78 to 310.22 mg/m^2d. These values appear to be between the average annual level and high level of sedimentary dust, which proves the well-known fact that burning of fossil fuel and automobiles are also the important anthropogenic sources of sedimentary dust, not only the gas pollutants in the air. The remaining two locations, 5 and 6, showed the similar mean values, i.e. 253.88 and 281.46 mg/m^2d, respectively.

3.2. Concentrations and Distribution of Metals in Sedimentary Dust

Sedimentary dust and corresponding metal concentrations at different locations are summarized in Table 5. and are shown graphically in Figures 4-5.

Table 5: Summary – statistics (mean± SD) sedimentary dust and metals concentrations (mg/m^2 d)

	1) Gas pump EP	2) Gas pump J.Kopex	3) Dzhenex center	4) Bus station Lukavac	5) Kulina Bana street 9	6) Cemetery	Total metal
SD	215.78±58.56	310.22±110.79	993.57±480.34	879.35±657.23	253.88±85.73	281.46±149.08	
K	34.200±0,036	113.320±0,038	187.920±0,030	118.420±0,034	46.280±0,029	77.440±0,035	577.580
Ba	10.868±0,009	30.600±0,010	32.100±0,009	11.512±0,007	21.64±0,009	8.690±0,006	115.410
Sr	1.306±0,009	4.646±0,010	7.336±0,009	7.714±0,012	1.452±0,009	2.864±0,011	25.318
Zn	12.116±0,095	17.080±0,105	101.500±0,100	13.636±0,095	7.760±0,095	3.728±0,105	155.820
Pb	0.228±0,018	0.044±0,019	0.032±0,018	0.218±0,015	0.000	0.000	0.522
Mn	0.492±0,114	1.140±0,120	3.862±0,122	2.700±0,098	0.680±0,104	1.346±0,118	10.220
Ni	0.228±0,061	0.296±0,064	2.240±0,058	0.864±0,064	1.794±0,061	0.816±0,066	6.238
Cr	0.120±0,087	0.168±0,089	1.242±0,099	0.498±0,092	0.188±0,080	0.448±0,088	2.664
Cu	0.336±0,042	0.496±0,045	0.954±0,049	0.804±0,048	0.484±0,044	0.490±0,044	3.564
Co	0.000	0.000	0.138±0,005	0.028±0,002	0.000	0.016±0,001	0.182
Cd	0.000	0.006±0,001	0.004±0,000	0.008±0,001	0.006±0,000	0.006±0,000	0.030
V	0.000	0.000	0.260±0,059	0.000	0.000	0.032±0,061	0.292
Total metal	**59.894**	**167.796**	**337.588**	**156.402**	**80.284**	**95.876**	**897.84**

N = 4 (SD), N = 3 (metals)

Figure 4: Concentration of K, Ba, Sr, Mn and Zn (ppm) in sedimentary dust

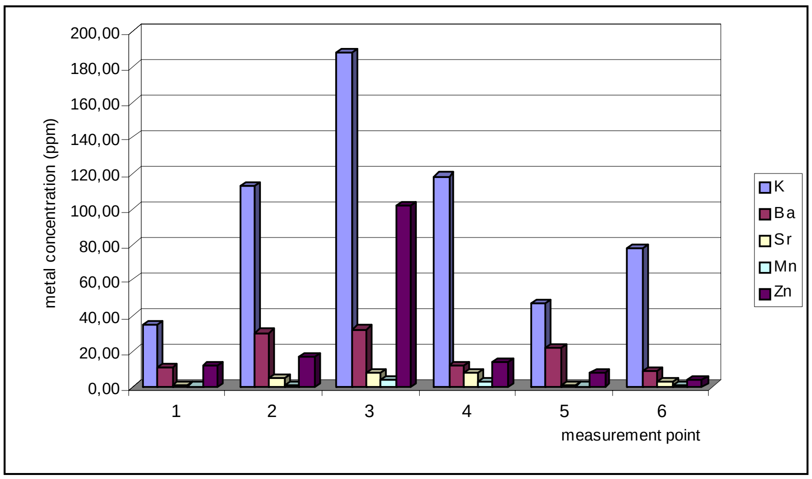
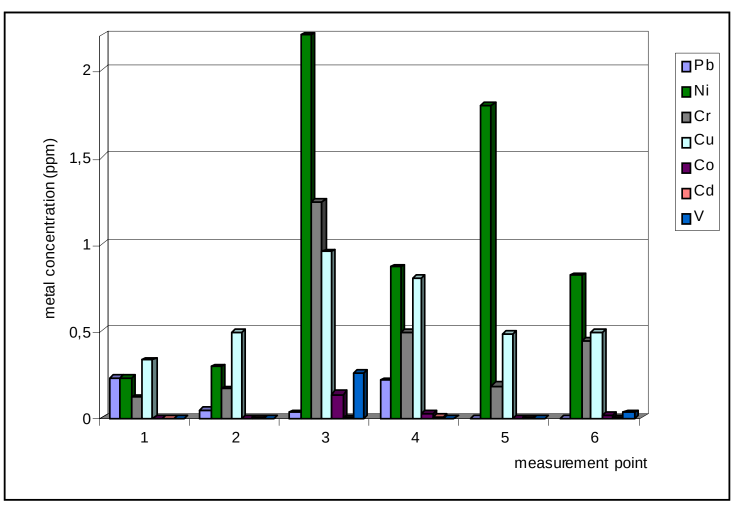
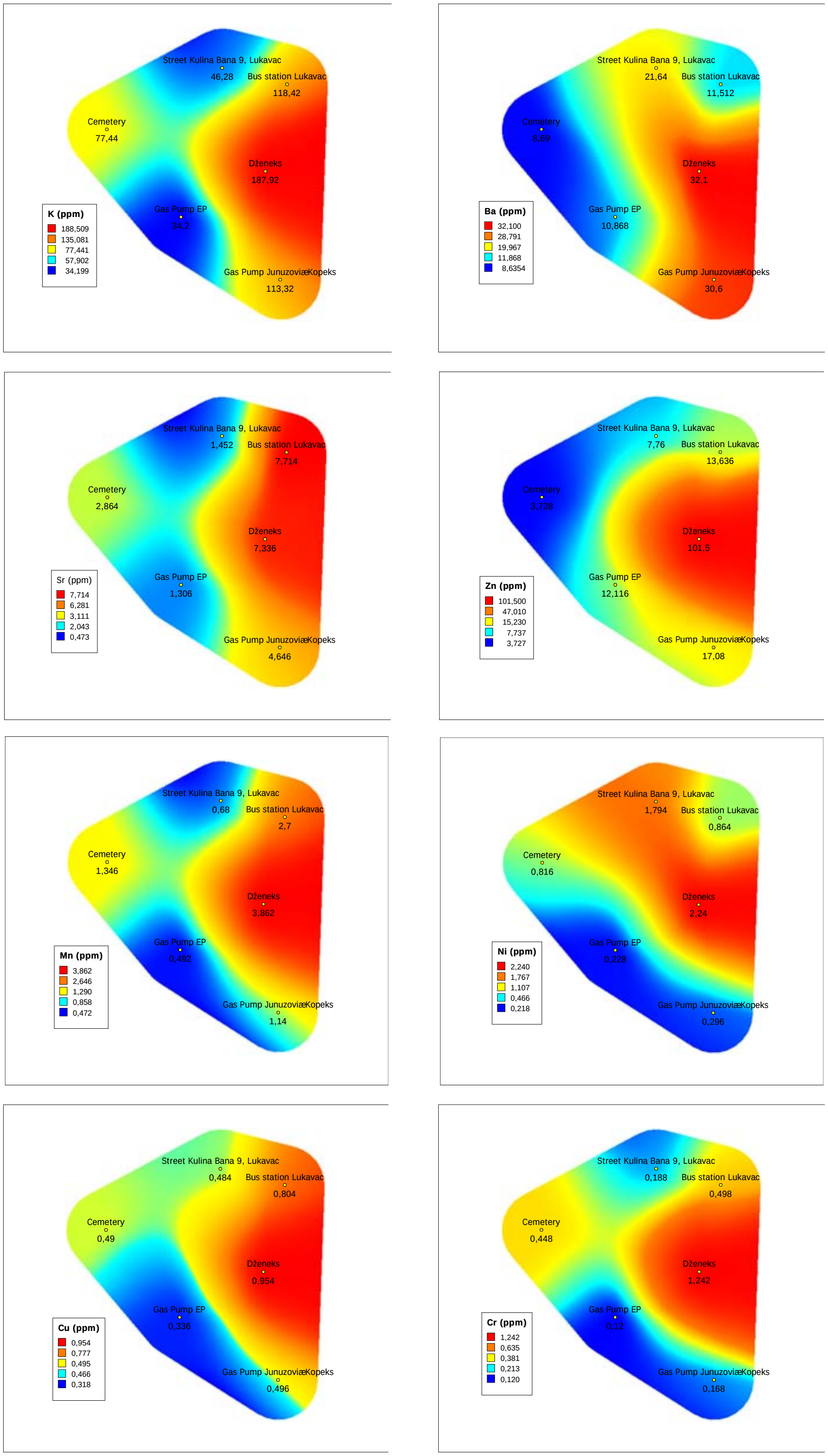


Figure 5: Concentration of Pb, Ni, Cr, Cu, Co, Cd and V (ppm) in sedimentary dust



Distribution of metals in sedimentary dust at different locations of Lukavac area of during four months is presented at Figure 6.

Figure 6: Distribution of metals in sedimentary dust at different locations of Lukavac area



Total mass of all the metals in each location and total mass of each metal at all the locations have been arranged in descending order as:

Metals: 3 > 2 > 4 > 6 > 5 > 1

Metal: K > Zn > Ba > Sr > Mn > Ni > Cu > Cr > Pb > V > Co > Cd

In the light of value of SD and mass of metals, it was observed that Dzhenex center was the most polluted and Gas pump EP was the least polluted areas of Lukavac. Total concentration of K is the highest and Cd has the lowest value. Mean concentration of K (187.920 mg/m^{2}d) at Dzhenex supermarket was the highest and the concentration of Cd (0.004 mg/m^{2}d) in the same location was the least. Correlation of SD with metals and intercorrelation among metals are shown in Table 6.

Table 6: Correlation matrix

	K	Ba	Sr	Zn	Mn	Pb	Ni	Cr	Cu	Co	Cd	V	SD
K	1.000												
Ba	0.614	1.000											
Sr	0.896*	0.339	1.000										
Zn	0.826*	0.656	0.586	1.000									
Mn	0.928*	0.368	0.905*	0.814*	1.000								
Pb	-0.187	-0.482	0.143	-0.192	-0.021	1.000							
Ni	0.482	0.457	0.295	0.673	0.586	-0.501	1.000						
Cr	0.863*	0.400	0.705	0.906*	0.936**	-0.217	0.715	1.000					
Cu	0.903*	0.402	0.911*	0.766	0.981**	-0.047	0.651	0.889*	1.000				
Co	0.853*	0.495	0.662	0.966**	0.904*	-0.184	0.717	0.983**	0.855*	1.000			
Cd	0.300	0.063	0.467	-0.180	0.273	-0.322	0.189	0.079	0.388	-0.051	1.000		
V	0.790	0.554	0.519	0.973**	0.803	-0.307	0.719	0.945**	0.741	0.978**	-0.159	1.000	
SD	0.857*	0.294	0.926**	0.729	0.969**	0.166	0.535	0.843*	0.977**	0.818*	0.293	0.682	1.000

* Correlation is significant at the 0,05 level (2-tailed)
* * Correlation is significant at the 0,01 level (2-tailed)

Correlation of SD with K ($r=0.896$, $p<0.05$), Sr ($r=0.926$, $p<0.01$), Mn ($r=0.826$, $p<0.01$), Cr ($r=0.843$, $p<0.05$), Cu ($r=0.977$, $p<0.01$) and Co ($r=0.818$, $p<0.05$) is also found to be positive and significant (Table 6). This indicates the linear dependence of metals on SD. In other words, increase or decrease in the concentrations of SD may also increase or decrease the concentrations of K, Sr, Mn, Cu and Co.

Correlation of K with Sr ($r=0.41$, $p<0.05$), Mn ($r=0.928$, $p<0.05$), Zn ($r=0.826$, $p<0.05$), Cr ($r=0.863$, $p<0.05$), Cu ($r=0.903$, $p<0.05$) and Co ($r=0.853$, $p<0.05$); Sr with Mn ($r=0.905$, $p<0.05$) and Cu ($r=0.911$, $p<0.05$); Mn with Cr ($r=0.936$, $p<0.01$), Cu ($r=0.981$, $p<0.01$) and Co ($r=0.904$, $p<0.05$); Zn with Mn ($r=0.814$, $p<0.05$), Cr ($r=0.906$, $p<0.05$) and Co ($r=0.966$, $p<0.01$); Cr with Cu ($r=0.889$, $p<0.05$), Co ($r=0.983$, $p<0.01$) and V ($r=0.945$, $p<0.01$); Cu with Co ($r=0,855$, $p<0,05$) and Co with V ($r=0.978$, $p<0.01$) are found to be positive and significant. The positive and significant association suggests that these metals are directly related to each other.

The most abundant elements in sedimentary dust (K, Ba, Sr, Zn and Mn) are the elements that are characteristic for industrial production in Lukavac because these elements are found in coal, fly ash and limestone (Table 7). Toxic heavy metals, including zinc, chromium, nickel, cuprum, cadmium, mercury and vanadium are also present in fly ash as a result of burning coal and raw materials.

Table 7: Concentrations of metals in the samples of coal, fly ash and limestone

	Metal concentration in samples (ppm)											
sample	**Ba**	**Sr**	**Zn**	**Pb**	**Mn**	**Ni**	**Cr**	**Cu**	**Co**	**Cd**	**V**	**Hg**
Coal	30.14	20.300	32.700	7.460	1.730	0.784	0.994	0.148	0.068	0.380	0.294	0.808
fly ash	12.328	7.210	3.836	0.190	3.732	2.382	1.994	0.220	0.158	0.184	0.510	0.020
limestone	1.006	5.738	0.000	0.000	0.268	0.108	0.282	0.014	0.000	0.000	0.018	0.000

K, Sr, Mn, Cr, Co and Cu show strong correlation with SD, which we can also see at the distribution diagrams of these metals at Figure 6. As conclusion, the above refractory metals are emitted from industry plants in the sampling area. The concentration of K, one of the characteristic elements of cement and soda production activity is considerably high, about 64 % of total deposition. Most of the eco-toxic metals (Hg, As, Pb, Cd and Cr) are volatile elements with a low boiling point and are largely associated with the fine particulate matter, which is only slightly retained by air-cleaning device. Pb, Cd and Zn concentrations are limited because of the well-known fact that these metals adsorbed on the surface of suspended particulate matter make it potentially dangerous dust. Although these metals do not show correlation with SD, their concentrations in SD are significant. The concentration of Pb was within the range of 0.218-0.228 mg/m^2d at stations 4 and 1, and in the range of 0.032-0.044 mg/m^2d at locations 3 and 2; at the remaining stations it was not registered. Lead pollution was highest at station 1 which is located close to the highway and station 4, near the bus station and residential area with heavy traffic. As compared to the limit values and the other stations, lead concentration exceeds national standard level value of 0.100 mg/m^2d. Atmospheric limit value is 0.5 $\mu g/m^3$ (1999/30/EC), expressed as an annual mean. Pb is present in all soils, rivers, lakes and sea water. Pb is in the form of halide salts in automobile exhaust, and is unstable and easily converted to oxides, carbonates and sulphates (Lone et al., 2006). Adsorbing on particles of sedimentary dust, lead is generally penetrated to the soil by aerial deposition along the road sides (Aksoy, 2008). The contamination of lead in the ambient air is mainly from the furnaces and also from automobiles. The main source of lead in the atmosphere for many years has been the use of leaded gasoline in vehicles (Simpson et al., 1994; Dixit et al., 2008). Since the lead content in fuels has been regulated during the past years, fuel burning activities and other industrial sources contribute in the ambient lead production. In the developing world although there are some regulatory measures to control the Pb emissions, it is still one of the major global environmental problem in many countries (Yang et al., 2000). When inhaled, lead is a probable human cancer-causing agent. Low-level lead intoxication can induce severe neurological and hematological effects to the exposed population and especially children. Also, lead affects the metabolism and accumulates in the living tissue, especially in the liver and kidneys. Lead replaces calcium in bones (Èetkauskaitë, 1999).

Cadmium is a toxic metal for most living species and it is well-known for causing cancer. When compared with the limit value for Cd (0.002 mg/m^2d) it is exceed in sedimentary dust at locations 2, 3, 4, 5 and 6. Cd concentration is found to be alarmingly high at the location near bus station, while it is almost equally distributed among the other locations. The EC limit values for Cd is 5 ng/m^3 (2004/107/EC). In rural areas, the yearly average of Cd ranges from <1 to 5 ng/m^3, in urban areas from 5-15 ng/m^3, in industrialized areas from 15 -50 ng/m^3, with much higher concentrations in the vicinity of processing plants. These concentrations are directly reflected in the precipitation of Cd with yearly deposition values ranging from 0.007 – 0.29 mg/m^3 in rural areas and 0.15 – 11 mg/m^3 in urban areas and 0.25 -73 mg/m^3 in industrial areas (G. Ziemacki, 1989). Cadmium and nickel compounds in SD mainly originate from coal and fuel oil combustion processes, metallurgical industry and road transport (2004/107/EC; Mugica et al., 2002). In animal experiments cadmium has caused cancer, birth defects and reproductive problems. Because of its high toxicity and great solubility in water Cd is a dangerous pollutant (Liu *et al.,* 2006).

The concentration of zinc in SD is alarmingly over the limit value of 0.4 mg/m^2d at all measuring sites. The results indicate that the maximum and minimum values of Zn were 101.5 mg/m^2d at Dzhenex center and 3.728 mg/m^2d at cemetery, respectively. There are many sources of Zn like fossil fuels, metal manufacturing and fertilization (Markert, 1993). Burning of coal in Thermal power plant in Tuzla and industries in Lukavac, releases considerable content of SO_2 in smoke gaseous. It chemically reacts with moisture from the air producing acid rain. Reaction of acid rain with the elements of galvanized gutters, fences, roofs, windows or other structural parts results in zinc melting and its adsorption on the dust particles. Zn is more reactive and mobile than Cu and Pb and moves through the soil. Zinc is also used in the lubricant additive zinc diethyldithiophosphate and is therefore likely to be incorporated into road dusts through oil leakage, and exhaust particles through oil combustion. A contribution from road traffic for Zn is therefore likely, but is not dominant. The total contribution of these sources, including industrial sources, made the Zn mean value reach an average value of 25.97 mg/m^2d in measured SD at all sites.

With respect to the other elements, Ni, Mn, Cr, Cu, Co and V it is difficult to conclude something because there are not the limit values for these elements in sedimentary dust at present. Sr, Mn, Cu and Co show linear dependence on SD, indicating the same sources contributing to both SD and trace metals. These metals are almost equally distributed among locations as sedimentary dust

(Figure 6), but the concentrations of Ni vary depending upon sources of its emissions. The urban area is influenced by vehicular population also, so the SD is rich in nickel, and the SD from Dzhenex center, being nearer to industry as well as residential place, is very rich in Ni (2.240 mg/m^{2}d). Nickel is commonly associated with the fine particulate matter fraction of ambient air samples with diameters ranging from 0.6 to 10 nm. The EC limit values for Ni is 2mg/m^3 (2004/107/EC). This element is mainly associated with fossil fuel use, oil burning and emissions from stationary and industrial sources. In global atmospheric emissions, total annual Ni emissions from anthropogenic sources are around 98000 and 30000 tons per year from natural sources (Ziemacki at al., 1989). The average Ni content in soils has increasing tendency. Compounds of nickel are susceptible for inducing carcinogenic effects in human, through inhalation. Continuous and prolonged exposure to nickel can produce dermatitis and disorders in the respiratory system. Ions of nickel enhance lipid peroxidation, reduce activity of glutathion peroxydase, lead to an increase of biologically active iron in tissues, induce DNA strand brakes, chromosome aberrations, formation of DNA adducts. Manganese shows strong correlations with Cu, Co and Cr. The concentration of manganese at stations 3 and 4 was at a maximum (i.e. 3.862 mg/m^{2}d and 2.700 mg/m^{2}d, respectively) where maximum SD values were also very high. At the remaining stations the Mn concentration was 0.492 – 1.346 mg/m^{2}d. Manganese is related to industrial processes and brake-drum abrasion was detected in the coarse particulates (Harrison et al., 1996). The suspension of crustal particles is possibly responsible for the ejection of manganese in the atmosphere. (Harrison et al., 2003) Since it has low volatility, Mn settles mostly in the immediate vicinity of its source of release. However, fine particles can be carried away. Manganese is a neurotoxic element that in continuous and prolonged exposure causes a neurological disease called manganism (WHO). The highest Cr pollution level was measured at station 3 was (i.e. 1.242 mg/m^{2}d) while at the remaining stations Cr concentrations were 0.120 – 0.498 mg/m^{2}d. The values at stations 1, 2 and 5 were close to each other. TA Luft limit value for Cr in SD is 250 μg/m^{2}d. Chromium is a naturally found in rocks, animals, plants, soil, and in volcanic dust and gases. It is usually occurs in two forms; chromium (III) and chromium (VI). The natural and essential one is the Cr (III), whereas Cr (VI) is generally by-product of industrial activities and considered to be more mobile and toxic (Paiva et al., 2009). The mobilization, subsequent uptake and the toxicity of the Cr depend on the metal speciation. Chromium in his hexavalent form causes cancer in humans. Compounds of Cr (VI) are known to have most toxic and carcinogenic effect on the bronchial tree (Manalis et al., 2005) and occupational exposure cause dermatitis, penetrating ulcers in the hands and forearms, perforation of nasal septum and inflammation of larynx and liver (Saraswathy and Usharani, 2007). As in the case of Mn, the range of cooper values is also associated with minimum and maximum values of SD, being 0.336 and 0.954 mg/m^{2}d, respectively. The highest Cu pollution was observed at location 3, i.e. 0.954 mg/m^{2}d, near to the industrial plants in the downwind direction. Emissions of atmospheric Cu are primarily due to metal production and other industrial processes. Copper is an irreplaceable microelement and serves as a cofactor for some oxidizes, oxygenizes and some other enzymes. Cattle need 6 to 12 mg and humans 2 mg of copper per day. However, if copper is present in excess concentrations, it catalyses formation of highly reactive oxygen species leading to lipid peroxydation, the lack of the reduced form of glutathion, enhancement of methemoglobin content (Èetkauskaitë, 1999). Generally, Cu accumulates in liver, in the lysosomes of hepatocytes. An increase in the level of Cu leads to respiratory irritancy. Moreover, elements such as Pb, Cu and Zn are mostly emitted into the atmosphere by heavy industry, coal burning, metallurgical smelters and automobile traffic (Pacyna, 1986). The increase in Pb and Cu can be explained by the heavy traffic and wind direction. The concentration of vanadium and cobalt at station 3 were at a maximum showing the behavior typical of fuel oil and coal burning. Vanadium is released into the air as fly ashes with a long atmospheric residence time (Ziemacki at al., 1989). Mercury and arsenic are not found in SD although coal and fly ash contain Hg. Because of its low boiling point and high temperature in industrial processes, Hg leaves plant by the waste gas and metal vapors condense onto the surface of the smallest particles or remain in vapor phase. The permissible emission of Hg to air (2004/107/EC) is very law (0,05 mg/m^3) due its toxicity. The amount of mercury emitted by a soda or cement manufacturing is proportional to the amount of mercury in the fuel and feed materials due to the volatile nature of mercury. The health risks associated with mercury are damage to the nervous system and deformities in infants exposed to mercury in the womb. Mercury causes birth defects (WHO). The standards ignore the synergistic effects of combinations of toxic air pollutants (Curtis *et al.*, 2006).

4. Conclusions

In the present study the concentrations of K, Ba, Sr, Mn, Zn, Pb, Cd, Cu, Cr, Co, V, Hg, As and Ni in sedimentary dust were measured by using ICP-OES method. The samples were collected by *Bergerhoff*-method in the urban and industrial area of Lukavac , Bosnia and Herzegovina, during the period July 2009 - November 2009. As sedimentary dust mass and its trace metals concentrations in the ambient air depends upon so many known and unknown factors, its monitoring is very important from the aspect of risk assessment to human health. The most significant factors for the distribution of pollutants are meteorological parameters of wind speed and direction. Presented results indicate that the environment in the Lukavac town is strongly polluted and the dominant sources of air pollution are industrial activities in Lukavac. Pollution problems increase in autumn and winter. At the sampling sites downwind of the industrial plant, the average concentrations of sedimentary dust exceeded the limit value of 350 mg/m^2d proposed by „Regulations on air quality". Also, concentrations for toxic heavy metals Cd and Zn were higher than the limited values. Vehicular traffic might also lead to an exceedance of the average limit value of Pb and Hg concentration. With respect to the other elements, there are not proposed limit values at present. But, there is positive and significant correlation of K, Sr, Mn, Cu and Co concentrations with the detected values of sedimentary dust, indicating the same source of pollution. Long-time exposure to toxic trace metals such as arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc even at low concentrations can be deleterious to human health. Total deposition dust and the deposition rates of most of elements emanates from the industry. Cr, Co and Cu suggest a coal burning signal released by industry. This is further confirmed by the presence of high concentrations of metals in sedimentary dust in the downwind direction. On the basis of emission data, a dust load of several tons per day is being emitted, which is too high and has to be brought down in a great percent. It will be possible to achieve better environmental conditions in terms of metal concentration, by the employment of high-efficiency control systems, such as scrubbers, fabric filters and electrostatic precipitators. Furthermore, the most important in the industrial air control are the performance and the maintenance of equipment. Air-cleaning devices influence much more for the retention of refractory elements than of the volatile elements. All attempts to increase filters efficiency should reduce the total mass emitted by stack, but it would not have a big influence for the volatile elements as Hg and As. It appears that the measures of improving the performance of technology equipment and pollutants control equipment should take parallel. For this reason, new basic criteria, in which first priority is given to the collection efficiency of fine particulate matter and gaseous pollutants, are strongly recommended.

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