REGIONAL LEVEL OF HEAVY METALS IN AMBIENT AIR OVER THE TERRITORY OF SLOVAKIA

Marta Mitošinková, Adriana Klimeková, Katarína Pukančíková

Slovak Hydrometeorological Institute, Jeséniova 17, 833 15 Bratislava, Slovak Republic

Regional level of heavy metals in ambient air has been monitored under the Slovak Hydrometeorological Institute in the network of the Slovak Republic consisting of five regional stations (Figure1): Chopok, Topolníky, Stará Lesná, Liesek and Starina. Four of these stations are EMEP stations (Figure 2) [1] and one at the same time also GAW/BAPMoN station. Concerning the stations, they have been established and put into operation gradually within 1978-1994, following the individual phases of EMEP monitoring programme under the 1979 UN ECE Convention on LRTAP.

Since 1985 eight heavy metals lead, manganese, copper, cadmium, zinc, nickel, vanadium and chromium in ambient air of rural areas have been included into the regular programme of the national network of the Slovak Republic (Figures 3 and 4, Table 1) [2]. The history of heavy metal measurements in ambient air began in 1980-1981. That time the Slovak Hydrometeorological Institute had started to determine copper, zinc, manganese, lead and cadmium in several stations, located in the most polluted industrial areas of central and east Slovakia, as well as in the capital of Slovakia, Bratislava. These determinations had been first extended for chromium, vanadium and nickel, but later on reduced. Since 1993, only lead and cadmium have been measured in polluted areas, in coincidence with the Clean Air Act 309/1991. Suspended particulate matter (SPM) is collected on membrane nitrocellulose filters either by low-volume samplers or by SPM collectors PPA60.

Figure 1 Network of regional stations in Slovakia - 2000

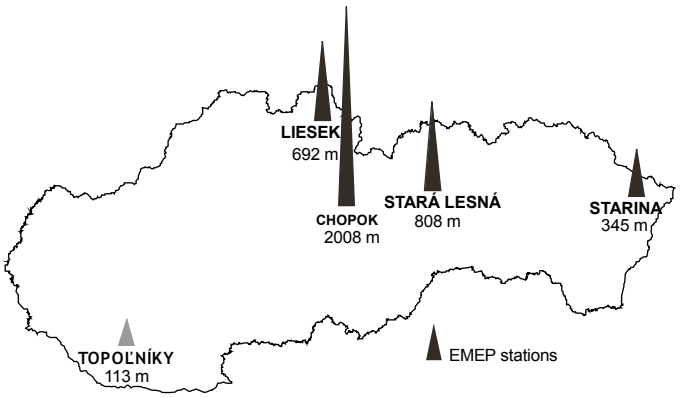
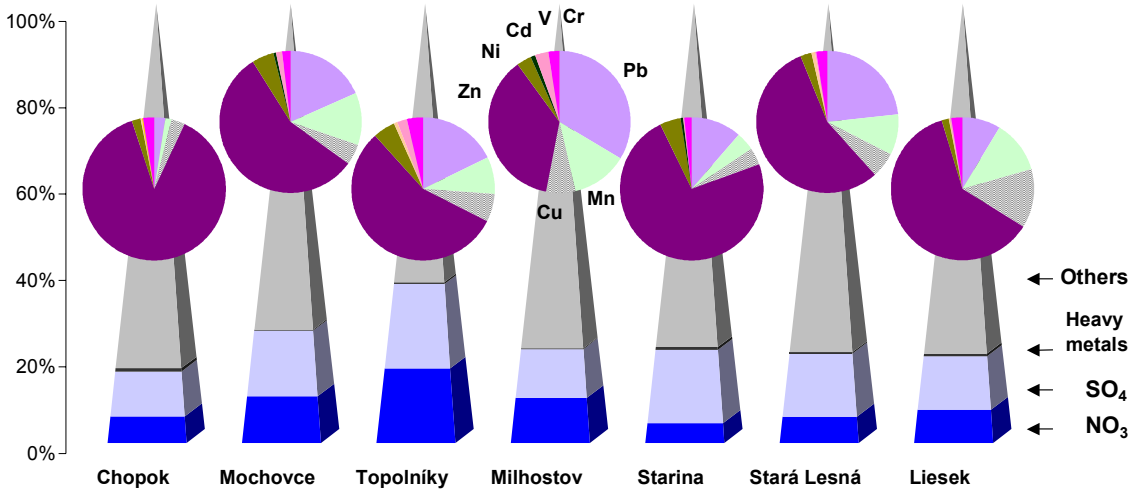


Figure 2 EMEP heavy metal monitoring stations - 1997

Figure 3 Heavy metals in ambient air – 1999

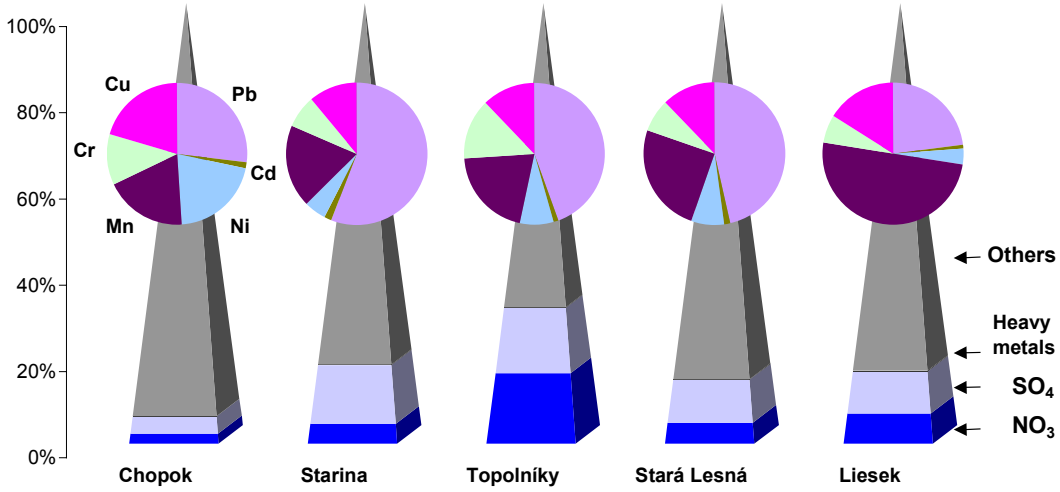


Station Milhostov has been in operation only till May 31, 1999 and Mochovce till December 31, 1999.

Table 1 Heavy metals in ambient air – 2000

	PM µg/m^3	Pb ng/m^3	Cd ng/m^3	Mn ng/m^3	Cu ng/m^3	Ni ng/m^3	Cr ng/m^3
Chopok	17.5	3.7	0.2	2.6	2.8	2.8	1.6
Stará Lesná	26.7	10.3	0.3	5.5	2.7	1.7	1.7
Liesek	32.7	11.8	0.4	25.6	8.3	1.9	3.3
Starina	24.5	18.9	0.6	6.4	3.8	1.7	2.5
Topolníky	30.5	17.7	0.5	8.2	4.9	3.1	5.5

Figure 4 Heavy metals in ambient air – 2000



By using low volume samplers, the sampling period is one week, while by using more efficient sampler PPA60, 3days. Samples are then assessed at monthly basis. Nitric acid and hydrogen peroxide are being used for digestion of filters in microwave oven. As standards the standard solutions of appropriate metal salts are used. For determination of heavy metals the method of atomic absorption spectrometry is used. Zinc is measured in flame, while lead, cadmium, copper, manganese, chromium, vanadium and nickel are measured in graphite atomizer.

Heavy metals zinc, iron, aluminum and manganese measured in precipitation and their regular programme on monthly basis have been introduced at all regional stations shortly after their putting into operation. In 2000 the measurements have been extended for lead and cadmium (Figure 5, Table 2). In addition, one station in the capital of Slovakia, Bratislava is also in operation. At present the samples are collected as "wet only" by WADOS collectors, apart from the station Chopok, where this collector had to be replaced by "bulk" collector (simple polyethylene bucket) because of very strong climate conditions at this mountainous station. Samples of precipitation are acidified with nitric acid prior to the determination by atomic absorption spectrometry. Zinc is measured in flame, while iron, aluminum, manganese, lead and cadmium in graphite atomizer.

Figure 5 Heavy metals in precipitation – 2000

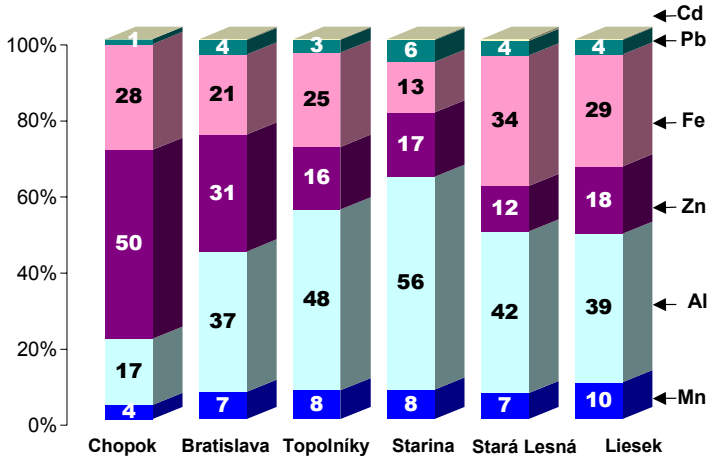


Table 2 Heavy metals in precipitation – 2000

	Prec. mm	Pb µg/l	Cd µg/l	Mn µg/l	Zn µg/l	Al µg/l	Fe µg/l
Chopok	1046	1.7	0.1	4.9	64.9	22.7	36.3
Stará Lesná	908	2.2	0.3	4.0	7.0	24.8	20.1
Liesek	888	2.0	0.1	4.9	9.0	20.0	15.1
Starina	882	3.0	0.2	4.1	8.9	29.4	7.0
Topolníky	431	1.7	0.1	3.8	8.2	23.7	12.3
Bratislava	638	2.5	0.2	4.8	20.6	24.6	14.1

Regional level of heavy metals in ambient air is generally smaller than that one of industrial. Mass portion of the sum of eight heavy metals in question accounts for less than 1% of the total SPM mass. Among the metals measured, zinc is most abundant, then lead, manganese, copper, chromium, vanadium, nickel and cadmium. The station in lowlands, Topolníky is to a certain degree influenced by the local sources and agriculture.

In Slovakia, the area most polluted by heavy metals is east part of Slovakia as a consequence of smelter operations, and mine that are located here. In spite of the measures aimed at the SPM reduction, lead and cadmium reach here high values. In east part of Slovakia also heavy industry, mainly metallurgy and engineering is responsible for high content of metals. In central Slovakia zinc and cadmium reach higher values as a consequence of zinc-ore smelter operation. The local sources burning solid fuels, power and chemical industry in central part of

Slovakia contribute also to the higher concentration of metals. On the other hand chemical industry, crude oil processing, petrol chemistry, power industry and traffic are dominant in the capital of Slovakia. The total distribution of heavy metal emissions in Slovakia does not fully reflect the regional level of heavy metals.

The decrease of majority metals in their concentrations, mainly those of lead, is well-documented at all regional stations of Slovakia (Figures 6 and 7). This effect has been significant taking into account traffic and gradual decrease of lead content in petrol since 1982 and nowadays by producing lead free petrol only. Last but not least the total decrease in production and decrease in burning of fossil fuels, which were substituted by natural gas also contributed remarkable to the lower concentrations of metals.

Concentrations of heavy metals in ambient air and precipitation for rural areas of Europe vary within the range of values listed in EMEP reports and are also in a good coincidence with our neighboring country, the Czech Republic.

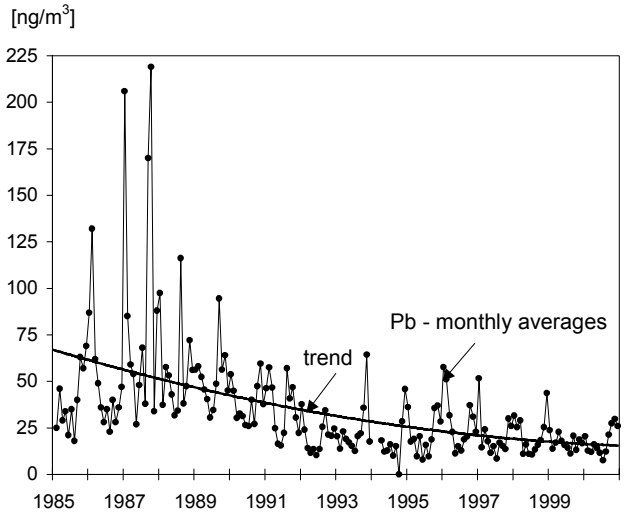


Figure 6 Pb in ambient air – Topolníky, 1985-2000

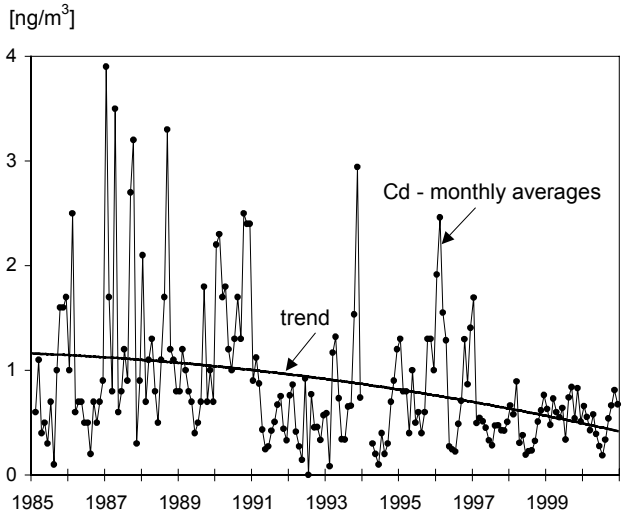


Figure 7 Cd in ambient air – Topolníky, 1985-2000

Last inter-comparison measurements on heavy metals in precipitation were carried out in 2000. Four samples were analyzed by participating laboratories on seven heavy metals (chromium, nickel, copper, zinc, arsenic, cadmium and lead) under the CCC (Chemical Coordinating Centre) EMEP in 1999 and 2000 [3]. Two samples were analyzed on seven heavy metals (manganese, iron, cadmium, copper, nickel, lead and zinc) under the WMO/ GAW 21st and 22nd Acid Rain Performance Survey [4, 5]. Concentrations of heavy metals within EMEP inter-comparison measurements were smaller than those ones of WMO/GAW and deviations from the true values were bigger (Figure 8, 9). The 21st and 22nd inter-comparison measurements of WMO/GAW do concern the year 1998 and 1999 (Figure 10). The results achieved were in a good agreement with the reference values. Information on quality of the precipitation measurements is also available upon the joint HELCOM-EMEP-PARCOM-AMAP inter-comparison measurements on heavy metals in precipitation [6], which were divided into an analytical and

field inter-comparison measurement part and included seven heavy metals chromium, nickel, copper, zinc, arsenic, cadmium and lead. The results from analytical part of the inter-comparison measurements showed that a majority of the participating laboratories reported deviation values within 25% from the theoretical values. In general, the results for lead were the best. The field part of inter-comparison measurements was carried out at the German EMEP station DE04 Deuselbach. The results achieved by the individual European countries were acceptable for lead, cadmium and zinc.

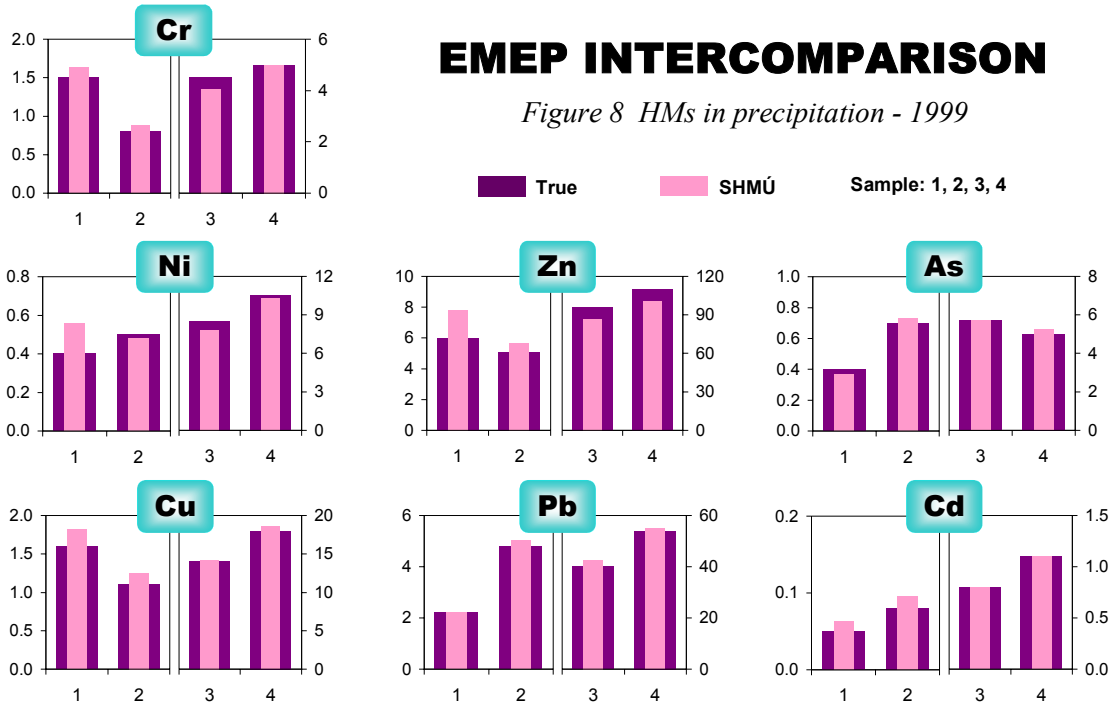


Figure 8 HMs in precipitation - 1999

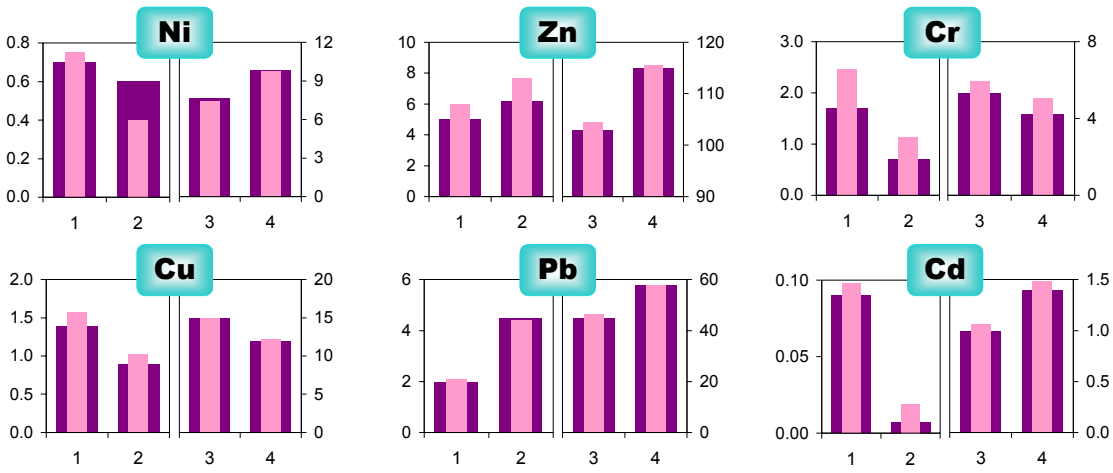


Figure 9 HMs in precipitation - 2000

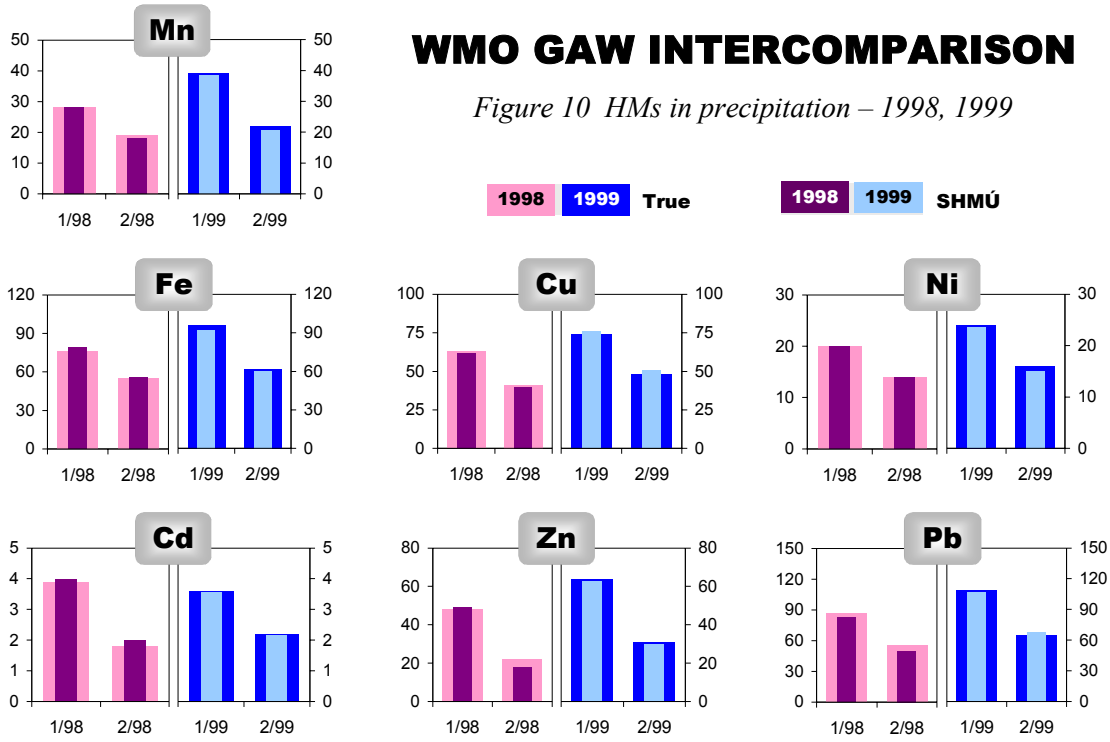


Figure 10 HMs in precipitation – 1998, 1999

References

[1] Hjellbrekke, A.G.- Berg, T.: Heavy metals and POPs within the ECE region 1997, EMEP/CCC-Report 7/99, NILU, Kjeller, Norway, pp.98.

[2] Report on Proceedings of the Workshop on the Assessment of EMEP Activities concerning Heavy Metals and POPs and their further Development, WMO Report No.117, Volume II/1996, Moscow, Russian Federation, pp 105.

[3] Berg, T.- Aas, W.: Analytical inter-comparison of heavy metals in precipitation 1999, EMEP/CCC-Report 8/00, NILU, Kjeller, Norway, pp.21.

[4] Coleman, L. T.- Galvin, J.P.- Mohnen, A.: Report of the 21st Inter-comparison of WMO/GAW Precipitation Chemistry Laboratories, WDCPC No.4/1999, Atmospheric Research Center, University of Albany, State University of New York.

[5] Coleman, L. T.- Galvin, J.P.- Mohnen, A.: Report of the 22nd Inter-comparison of WMO/GAW Precipitation Chemistry Laboratories, WDCPC No.5/2000, Atmospheric Research Center, University of Albany, State University of New York.

[6] Winkler, P.- Roider, G.: HELCOM – EMEP – PARCOM - AMAP Field Inter-comparison of Heavy Metals in Precipitation 1995, DWD, Meteorological Observatory Hohenpeissenberg, pp.150.