A CHEMICAL SPECIATION OF TRACE ELEMENTS IN THE TSP LONG-TERM MONITORING AT MONTENEGRO COAST

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Abstract

Levels of total suspended particles (TSP) were monitored from 1995 to 2000, every 6 day at stations located on the Montenegro coast of the South Adriatic sea. Collected deposits are 24-hourly samples wich were taken according to meteorolgical time. Particles were collected using a high-volume sampling system with glass fiber filter. Employing AAS equipped with hydride vapor system the concentrations of trace elements were determined in the particles. TSP concentrations ranged from 1.4 to 106.6 μgm^{-3} (mean 36.77 $\pm$ 21.00), Cd from 0.2 to 2.1 ngm^{-3}, Co from 0.5 to 3.8 ngm^{-3}, Fe from 0.7 to 3813.6 ngm^{-3}, Ti from 10.0 to 371.0 ngm^{-3}, and Mn from 0.2 to 74.6 ngm^{-3}, Cr from 0.6 to 7.4 ngm^{-3}, Cu from 0.3 to 53.0 ngm^{-3}, Ni from 1.0 to 85 ngm^{-3}, Pb from 1.0 to 243.0 ngm^{-3}, Hg from 0.01 to 20.63 ngm^{-3}, Se from 0.02 to 9.15 ngm^{-3}. One of the most characteristic sources of natural PM affecting the Southern Europe is the dust, long range transported from the North Africa (Sahara and Sahel desert). The impact of the anthropogenic emission are showed.

Introduction

The Mediterranean Sea is a small enclosed basin, which is susceptible to dust transport from desert sources in North Africa (Sahara) and the Middle East (the Arabian Peninsula and Syria) on its periphery. The dry climate and the scarcity of precipitation in the Mediterranean basin allow a long residence time of aerosol particles in the atmosphere and favor their transport on a regional scale (1,2,3).

Within the framework of the Mediterranean Action Plan, adopted by the governments of the region, a long-term program for pollution monitoring and research the Mediterranean Sea (MED POL phase II) was initiated in 1981. Monitoring of pollutant transport to the Mediterranean Sea through the atmosphere is one of the four components of MED POL phase II for which the World Meteorological Organization (WMO) has been initiating relevant activities. Airborne pollution monitoring was prepared 1987 and organized in a network of stations along the Mediterranean coast. The former Federal Republic of Yugoslavia (FRY) was one of the participants of this program and in 1990 initiated the experimental phase that is still on going (8,9).

The sampling station is located at the entry of the Boka Kotorska Gulf (Fig. 1) in the eastern suburban of the town Herceg-Novi ($18^0$33' N, $42^0$27' E). The sampling site is situated very close to the coast of the Adriatic Sea, only 10 m away, and there are no obstacles or PM sources between the coast and the station.

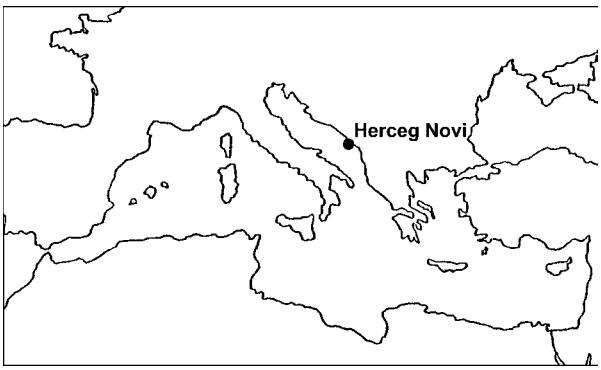

Fig. 1 The sampling site

The seaside of Montenegro has a Mediterranean climate. Herceg-Novi is a tourist town in Montenegro with about 25,000 inhabitants. Temperatures from 7.0 to 8.5 ^{0}C in January and 23-25 ^{0}C in July characterize the climate of Herceg Novi. The average annual precipitation is 2016 mm (L m^{-2}) of which only 10% falls in the summer months. The average relative humidity is about 70% with moderate fluctuations during the year. The prevailing wind directions are NE/N/NW in the winter and SE/S/SW in the summer.

Methodology

The data set from 4/5 January 1995 to 31 May/1 June 2000 was chosen for the analysis. 24-h samples were taken from 8am to 8am according to MET time a 1-in 6-day sampling schedule. The PM samples were collected on boron-silicate glass fiber filters (Schleicher&Schuell, 20 cm x 25 cm) by high-volume sampler (Aerosol Sampler AQUERO, model 400XT) at a flow rate of 50 m^3h^{-1}(5).

TSP were determined by gravimetric method. For determination of trace elements in the TSP, a fraction 1/2 from each filter was prepared. The filters were digested in the closed teflon vessels on the sand bath at 130 $\pm$ 10^{0}C. After put filter in the teflon bottles added 15 ml HNO_3 (Fluka-high purity), botles were cover and put on a sand bath to refluxing for 10 – 12 hours. After reduce the acid volume down to approximately 10 ml added 5 ml of concentrated HF (Fluka-high purity) and allowed refluxing for 6-8 hours. Afterwards added 5 ml of concentrated HNO_3 and repeated the evaporation until nearly dry and the white fumes of HF no longer be visible. The residue dissoved with 1% HNO_3 to a 50 ml. Employing AAS –SpectrAA 55 Varian equipped with hydride vapor system the trace elements were determined. By AAS determined Cd, Co, Cr, Cu, Ni, Pb, Mn, Fe and Ti while Hg and Se determined by AAS hydride vapor system.

The available PM data sets were analyzed using the SPSS 10.0 statistical program.

Results

Table 1 shows a minimum, a maximum and the annual mean values with standard deviations of the result measurements under all meteorological conditions. The values equal or smaller than detection limits were arbitrarily taken as the half of detection limit.

The concentration dataset on 11 elements and PM (TSP) in 252 air samples was evaluated by Principal Component Analysys on the basis of the Kaiser criterion (Table 2). PCA shows four significant factors extracted by *varimax* orthogonal rotation that enabled a better look into structure of the data. Factor 1 shows a high level of TSP, Cu, Pb, Ti, Fe and Mn. Such a feature suggests a common emission source for these elements, probably the strong influence of superficial crustal material resuspension. Origin of Fe, Mn and Ti is principally from priority of erosion crustal material of soil surface while presence Cu and Pb in Factor 1 can be consequence the rising disposaled material from soil surface including primary elements.

Factor 2 represents Cr and Ni, Factor 3 Cd and Se and Factor 4 Co and Hg. For other elements suggest the existence of additional 3 groups of emission sources: II (Cr, Ni), III (Se, Cd), and IV (Co, Hg). All these point to contributions of several groups of emission sources.

Table 1 The measured values of PM and the trace elements in the period 1995-2000

		N	Minimum	Maximum	Mean	Std. Deviation
TSP	($\mu g\ m^{-3}$)	252	1.4	106.6	36.77	21.00
Cd	($ng\ m^{-3}$)	252	0.2	2.1	0.297	0.25
Co	($ng\ m^{-3}$)	252	0.5	3.8	0.76	0.51
Cr	($ng\ m^{-3}$)	252	0.6	7.4	2.60	1.73
Cu	($ng\ m^{-3}$)	251	0.3	53.0	4.81	4.69
Ni	($ng\ m^{-3}$)	252	1.0	85.0	4.36	9.18
Pb	($ng\ m^{-3}$)	252	1.0	243.0	56.08	46.00
Hg	($ng\ m^{-3}$)	251	0.01	20.6	2.883	3.34
Se	($ng\ m^{-3}$)	227	0.02	9.1	0.143	0.63
Ti	($ng\ m^{-3}$)	251	10.0	371.0	58.80	48.80
Fe	($ng\ m^{-3}$)	251	0.7	3813.6	501.73	405.03
Mn	($ng\ m^{-3}$)	251	0.2	74.6	8.29	9.23
Valid N (listwise)		226				

Table 2 Rotated Component Matrix of PCA

	Factors			
	1	**2**	**3**	**4**
TSP	**0.787**	-0.116	-0.037	0.160
Cd	-0.061	0.200	**0.795**	0.095
Co	0.174	-0.008	0.015	**0.742**
Cr	0.336	**0.694**	0.080	-0.152
Cu	**0.587**	-0.145	0.124	-0.156
Ni	-0.082	**0.702**	-0.036	0.031
Pb	**0.479**	0.192	0.241	-0.530
Hg	0.147	0.418	0.144	**0.503**
Se	0.063	-0.133	**0.752**	-0.069
Ti	**0.729**	0.325	-0.022	0.091
Fe	**0.853**	0.168	-0.075	0.014
Mn	**0.811**	0.227	0.047	0.314

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
Rotation converged in 6 iterations.

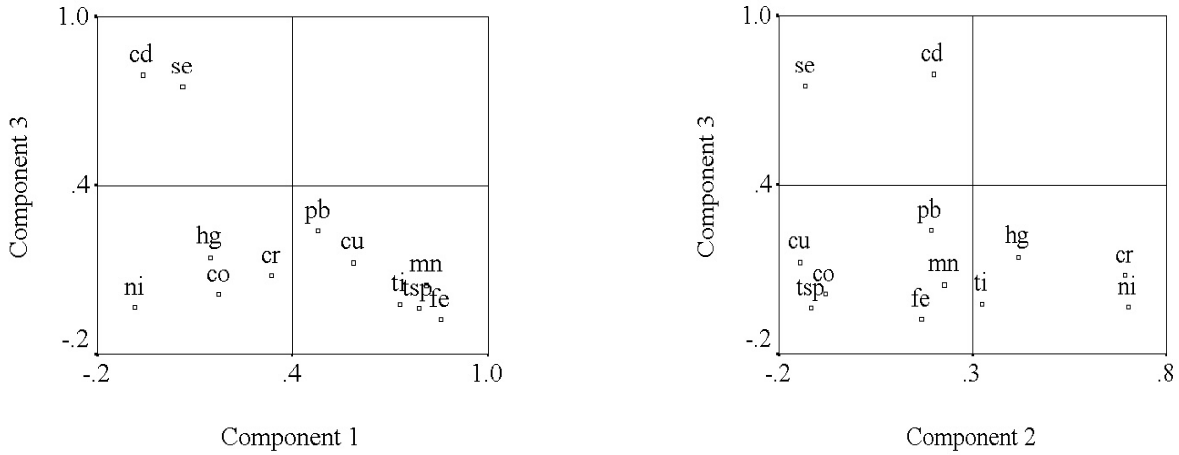

Fig. 2 The plot of the first, second and third PC weights

Fig. 2 shows groups of components for each other in relationship. It is obvious that crustal (Fe, Mn and Ti) elements are closely associated that is indicated emission of local resuspension. The several trace elements (Pb, Cu and Co) follows the crustal elements as consequences of a dry deposition at surrounding from various local and regional emission sources and than across resuspension are return in the air. Nevertheless, only Cd and Se located in the one separate quadrant. They have one common, likely local emission source. The group of the trace elements Hg, Cr and Ni originatings from particularly sources, differs of primary. Theirs emission sources can be regional or they come over long-range transport from remote areas (6,7).
The statistical output (Fig. 3) showed that Fe, Mn and Ti have a high degree of association for each other, and also have a high correlation degree ($r = 0.686$ and $p < 0.001$ for Fe-Mn, $r = 0.677$ and $p < 0.001$ for Fe-Ti).

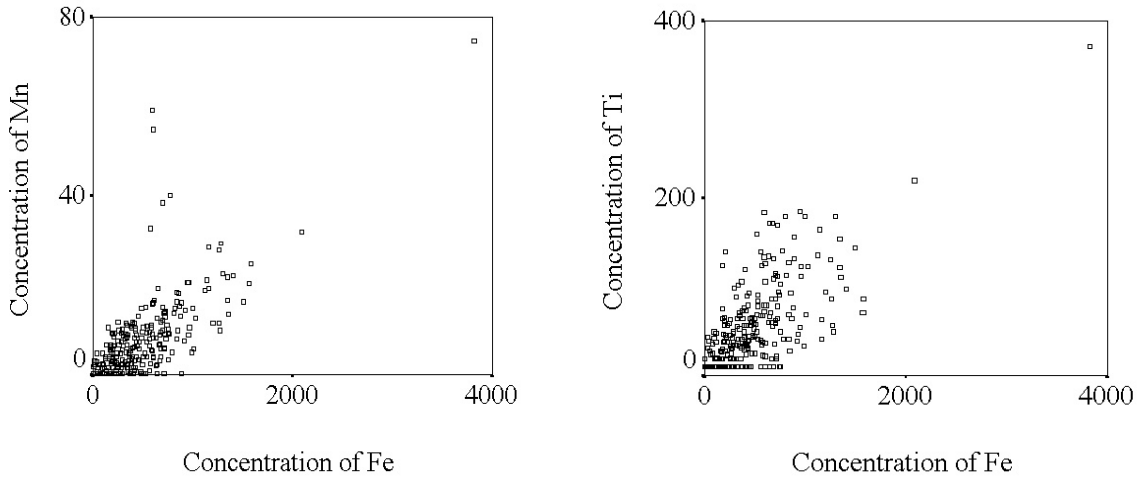

Fig. 3 The scater plot of correlations beetwen Fe- Mn and Fe-Ti respectively

The coefficient of correlations between TSP and Fe, Mn, Ti respectively ($r = 0.528$ and $p < 0.001$ for TSP-Fe, $r = 0.634$ and $p < 0.001$ for TSP-Mn and $r = 0.387$ and $p < 0.001$ for TSP-Ti) are higher versus coefficients of TSP-Cu and TSP-Pb respectively ($r = 0.260$ and $p < 0.001$ for TSP-Cu and $r = 0.282$ and $p < 0.001$ for TSP-Pb).

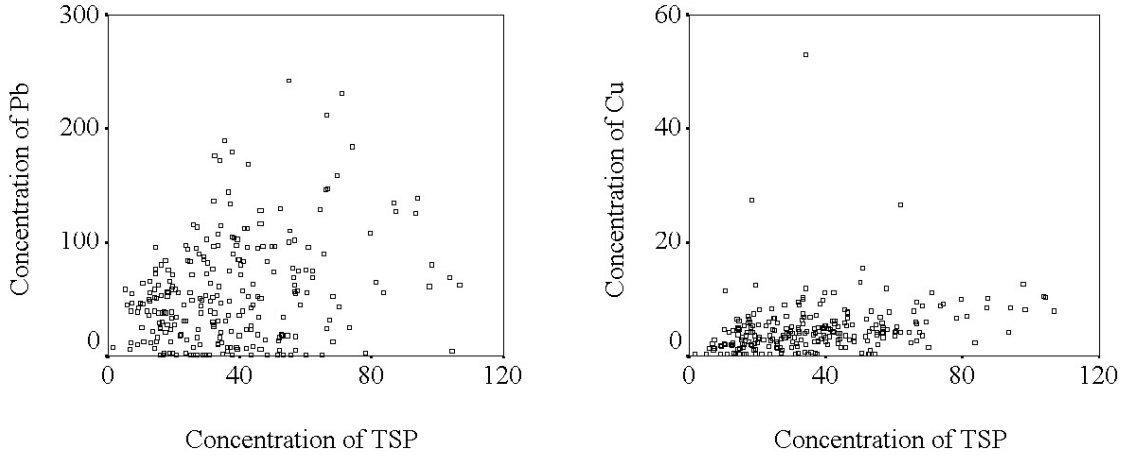

Fig. 4 The scater plot of correlations beetwen TSP-Pb and TSP-Cu respectively

Conclusion

This analysis of the trace element in TSP sampled at station Herceg Novi showed the existence of several influences or sources. There is one dominated source for association I (Fe, Mn, and Ti), most probably the local emission source of crustal material resuspension (4). The other investigated elements are arrangement into three groups: II (Cu, Cr and Pb). III (Hg, Co, Ni,) and IV (Se and Cd) – indicating the contributions of several emission sources different strengths and reaches. Besides local emission sources results indicated transport of trace elements from regional scale (most likely Ni) and moreover transport from remote areas, from African deserts or other the areas e.g. active volcanoes in northern Italy, Stromboli. Long-range transport is showed by a few outliers (10) of Fe, Mn and Ti in data of set that is coming from SSW direction across open sea.

Acknowledgements

We thank to the Ministry of Science, Technology and Development of Serbia for financial support (Project 1449). We thank moreover to the Hydrometeorological Service of ex-FR Yugoslavia for supporting this research, especialy colleagues Tanja Vuković and Dragan Đorđević.

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