PHYSICAL CHEMISTRY 2006

Proceedings

of the 8th International Conference on Fundamental and Applied Aspects of Physical Chemistry

September 26-29,
Belgrade, Serbia

ISBN	86-82139-26-X
Title:	Physical Chemistry 2006. (Proceedings)
Editors	Prof. dr A. Antić-Jovanović
Published by:	The Society of Physical Chemists of Serbia, Studentski trg 12-16, P.O.Box 137, 11001 Belgrade, Serbia
Publisher:	Society of Physical Chemists of Serbia
For publisher:	Prof. dr S. Anić, president of the Society of Physical Chemists of Serbia
Printed by:	"Jovan" Printing and Published Comp; 250 Copies; Number of Pages: x + 442; Format B5; Printing finished in September 2006.
Text and Layout:	Aleksandar Nikolić

250 – copy printing

HEAVY METAL CONTENT OF PM10 AND PM2.5 WITHIN URBAN AREA OF BELGRADE

S. Rajšić[1], Z. Mijić[1], M. Tasić[1], D.Đorđević[2], M.Radenković[3] and J. Joksić[3]

[1]*Institute of Physics, Pregrevica 118, Belgrade (rajsic@phy.bg.ac.yu),*
[2]*ICTM-Centre of Chemistry, Njegoševa 12, Belgrade, Serbia*
[3]*Institute for nuclear sciences-Vinča, PO.Box 522, Belgrade, Serbia, Serbia*

Abstract

An assessment of air quality of Belgrade was performed by determining the trace element content in airborne PM10 and PM2.5 in two years period. Samples were collected at two locations in a heavy polluted area. The concentrations of Al, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn were determined with AAS. Results indicated that the ambient concentration of Zn in the PM10 and PM2.5 was the highest (1389.18 and 1998.00 ng m^{-3} respectively). Also, the highest enrichment factor (EF) value was obtained for Zn, folowing with high EF for Cd and Pb in PM10, reflecting the importance of anthropogenic inputs. The limit values of toxic trace elements from WHO and EC Air quality guidelines were not exceeded except for Ni.

Introduction

Besides natural emissions, heavy metals are released to the atmosphere by the human activities such as combustion of fossil fuels and high temperature industrial activities. Trace metals are found in almost all aerosol size fractions what may have a great effect on the toxicity of metals when inhaled because the degree of respiratory penetration is particle size dependent [1].

Sampling of particulate matter with aerodynamic diameter D<10 μm, PM10 and D<2.5 μm, PM2.5 was conducted at two sites in the very urban area of Belgrade during the June 2003 - July 2005. Suspended particles were collected on Pure Teflon and Teflon-coated Quartz, Whatman, (47 mm diameter) filters, using the air sampler Mini-Vol Airmetrics Co., Inc., (5 l min^{-1} flow rate). The duration of each sampling period was 24 hours. Particle mass was gravimetrically determined and filter samples were digested in 0.1N HNO3 on ultrasonic bath and metals were analyzed with AAS.

Extraction with dilute acid has been used for the evaluation of elements which can become labile depending on the acidity of the environment. This procedure gives the valid information on the extractability of elements, because the soluble components in aerosol are normally dissolved by the contact with water or acidic solution without us in the actual environment [2].

During the sampling, conventional meteorological parameters were regularly recorded at the Meteorological Station of the Hydro-Meteorological Institute of Republic of Serbia, located inside central urban area.

Results and Discussion

The total mean concentrations of individual metals detected are shown in Table 1.

Table 1. Statistical parameters of heavy metal concentrations in PM10 (ng m^{-3})

	Pb	Cu	Zn	Mn	Fe	Cd	Ni	V	Al	Cr
N	210	210	210	210	210	210	210	210	210	167
mean	46.5	71.3	1389.2	20.8	1462.9	1.4	17.7	36.6	873.8	10.2
st.dev	128.5	118.7	2313.4	15.9	1911.9	2.2	17.7	48.8	914.1	11.4
max	1525.0	947.5	17239.6	72.7	20283.0	17.7	107.7	282.4	6104.2	58.0
min	0.5	0.2	2.1	0.2	0.5	d.l.	0.4	0.6	2.1	0.1
median	19.1	42.4	400.2	14.6	746.7	0.5	12.0	10.8	598.5	7.5
98 perc.	322.4	556.6	7018.3	62.4	5749.1	7.9	71.6	166.2	4126.9	46.3

The results indicated that the Fe content was the highest in the suspended particles with diameter less than 10 µm. Concentrations of Zn were, also, very high.
The highest mean concentration in PM2.5 was for Zn (1998 ng m^{-3}). Zn is reliable tracer of unleaded fuel and diesel oil motor vehicle emissions. Besides, Zn could be released from tires friction. Cu showed relatively high mean value of 71.3 in PM10.

Table 2. Statistical parameters of heavy metal concentrations in PM2.5 (ng m^{-3})

	Pb	Cu	Zn	Mn	Fe	Cd	Ni	V	Al	Cr
N	64	64	64	64	64	64	64	64	64	64
mean	21.0	20.8	1998.0	15.2	1081.2	0.9	28.4	59.8	1180.3	6.2
st.dev	27.0	19.2	1846.4	13.7	1360.3	1.2	43.1	56.3	1657.4	3.8
max	193.9	99.6	6642.4	50.7	5996.5	4.8	315.0	248.5	7875.0	26.0
min	0.5	0.2	115.2	2.1	49.7	d.l.	0.4	5.2	159.1	1.6
median	13.5	17.4	1153.3	10.1	488.4	0.4	17.3	50.2	500.7	5.9
98 perc.	66.8	80.6	6101.7	47.9	5380.6	4.1	107.9	208.7	7307.3	13.2

This trace element is associated with industrial activities, but in urban areas road traffic (diesel engines and wearing of break vehicles) could be mainly source [3]. Vanadium is related to oil combustion almost 100%. The obtained mean value was 60.0 ng m^{-3} in PM2.5. Ni is mainly associated with fossil fuel use, and emissions from industrial sources. Mean Ni concentration of 28.4 ng m^{-3} in PM2.5 fraction was above the critical value. Mean concentrations of Pb, Cd, V, and Mn did not exceed the current air quality guideline values during three-years sampling period.

The Directive EU Air Quality setting a Pb annual limit value of 500 ng m^{-3}. The mean annual concentration proposed for As is 6 ng m^{-3}, 20 ng m^{-3} for Ni and 5 ng m^{-3} for Cd, all measured in the PM10 particulate fraction [4]. WHO Air Quality Guidelines includes an annual tolerance concentration of 150 ng m^{-3} for Mn, and for V the proposed 24-h concentration is 1 µg m^{-3} [5].

The results of enrichment factor (EF) can provide useful evidence for the sources identification of the elements in aerosols. The EF closed to unity suggests that the element is dominantly from crustal materials. EF of Zn was the highest (678 for PM10 and 1320 for PM2.5); EF of Cd (237 for PM10 and 196 for PM2.5) and EF of Pb with the value 122 for PM10 and 75 for PM2.5; intermediately enriched (EF between 10 and 100) were Cu, V and Ni.

Conclusion

The first results of heavy metals measurements in PM10 and PM2.5 in the urban area of Belgrade showed that concentrations for most metals remained below assessment thresholds and legislated limit value, except for Ni in PM2.5 fraction. A very high Zn contents were found for course and fine particles. It should be noted, that obtained concentration levels were, probably, lower than total metal contents in particles because a mild acid digestion was applied. The main sources of heavy metals in PM10 and PM2.5, suspended in Belgrade ground-level atmosphere, were traffic emission, road dust resuspension and emission from stationary combustion of fossil fuels (mostly for heating).

References

[1] Espinosa, Rodriguez, De la Rosa, Sanchez, Atmospheric Environment, 2002, **36**, 773-780.
[2] T.Kyotan , M.Iwatsuki, Atmospheric Environment, 2002, **36**, 639-649.
[3] J.M.Pacyna, E.G.Pacyna, Environment Review, 2001, **9**, 269-298.
[4] EC, European Commission, 2003.
[5] WHO, Air quality Guidelines, 2000.