J. Int. Environmental Application & Science, Vol. 2 (3&4): 51-56 (2007)

The determination of some trace elements (Pb, Cd and Zn) in fine particles PM_{10} in Mitrovica urban atmosphere[#]

Afrim Syla[1,*], Agron Veliu[1], Kadri Berisha[2], Emin Karakashi[2], Islam Fejza[2]

[1]*MESP – Ministry of Environment and Spatial Planning, Prishtina-Kosova*
[2]*Faculty of Mining and Metallurgy – Mitrovica, Kosova*

Received 20 November, 2007

Abstract: The city of Mitrovica, approximately 40 km north of Prishtina, was the site of one the largest lead smelters in Europe. The present environmental situation in Mitrovica, put as in front of the responsibility to act more rationally towards nature and to be more responsible towards the protection of the environment for future generations. The protection lack of the environment during the last ten years, as well as the conflict in Kosova is the origin of huge problems regarding present environmental situation in Mitrovica (Kosova). Mitrovica has its air divided in two kinds, speaking in quality terms: Air above rural and mountainous zones, which is clean. Air above the city centre urban and nearby different plants, which is more polluted. Urban air contains dust particles and gases, added on it is as results of normal activity of the city and industries in them. Mitrovica can be cited as one of the capitals of Europe with worst air pollution. Exposure to airborne particulates PM_{10} and $PM_{2.5}$ containing low concentrations of heavy metals, such as Pb, Cd and Zn, may have serious health effects. However, little is known about the specification and particle size of these airborne metals. Fine and PM_{10} particles size with heavy metals in aerosol samples from the Mitrovica urban area were examined in detail to investigate metal concentrations and speciation. The crystal structures of the particles containing Pb, Cd and Zn were determined from their electron diffraction patterns by XRF methods.

***Keywords**:* Atmospheric particulates, heavy metals, PM10, PM2.5.

Introduction

Atmospheric particles aerosols are some of the key components of the atmosphere. They influence the energy balance of the Earth's surface, visibility, climate, human health and environment as a whole. According to World Health Organization (WHO), ozone, particulate matter, heavy metals and some hydrocarbons present the priority pollutants in the troposphere. The results of the long-term studies confirm that the adverse health effects are mainly due to particulate matter, especially small particles–less than 10 microns in diameter, PM_{10}. According to the 1999/30/EC Directive, the countries-members are obligated to reduce the emission of the particles in urban areas by some 50% over the existing levels in order to meet the health-based limit values by 2005 and 2010. Within the European programme for monitoring and evaluation of the long-range transmission of air pollutants (EMEP), measurements of PM_{10} and heavy metals, as highly toxic species have been introduced.

Atmospheric Aerosols

Atmospheric particles are a complex mixture of inorganic and organic substances, suspended in the atmosphere as both liquids and solids. They vary also in shape, chemical

[*] Corresponding author: *e-mail: afrimsyla2002@yahoo.com, Tel: +37744147473; Fax: +38138540842*

[#]This study has been presented at "13th Int. Metallurgy & Materials Congress, November, 2006, Istanbul-Turkey.

composition and optical properties. Particle size is one of the key parameters that govern the transport and removal of particles from the air, their deposition within the respiratory system and is associated with the chemical composition and sources.

Atmospheric particles generally occur in two distance modes: the fine (<2.5 µm) mode and the coarse (2.5-10 µm) mode.

Fine particles have an aerodynamic diameter less than 2.5 µm ($PM_{2.5}$) and differ from coarse particles in origin and chemistry. The fine or accumulation mode is ascribed to growth of particles from the gas phase and subsequent agglomeration. This fraction is composed of varying amounts of sulphate, small amount of sail dust and trace species (Pb, Cd, Ni, Zn, Mn, Fe, *etc*.). This size fraction is generally man-made.

Coarse particles are mainly formed by mechanical forces such as crushing, grinding, and abrasion of materials of geological origin. Generally coarse particles normally consists of alumina-silicate and other oxides of crystal elements, and major sources including fugitive dust from roads, industry, construction and demolition, fossil fuel combustion, *etc*.

Anthropogenic Sources

"Road transport"

Particulate emissions from road transport come up as direct emissions from vehicle exhaust, tire and brake wear and re-suspension of road dust and in urban areas, and it is the major sources of particles. The chemical composition of these particles may also be very different from those derived from combustion. Particulate matters also enter the atmosphere from dust on the road surface which is entrained by the motion of the vehicle along the road.

"Stationary combustion sources"

Stationary combustion sources involve domestic sources, large combustion sources (power stations running with coal, oil and gas) and industrial plants.

Physical Characterization of Aerosols

Physical characterization of aerosols atmospheric particles includes determination of size distribution, shape, optical features, elemental, molecular and isotope structure. All these properties profoundly influence the behaviour of atmospheric particles and their effects on health and environment. The effect of particle size is strongly dominant as it influences the aerodynamics, respireability, lifetime and removal from the atmosphere. The particle shape controls the toxicity and respireability.

Chemical Characterization of Particles

It is well established that chemical contents influence the transport and transformation processes of atmospheric particles; thus chemical characterization of atmospheric particles has an important role in better understanding of their behaviour and influence. The majority of particles of industrial origin contain significant quantities of some potentially dangerous trace elements. As the result of condensation and adsorption processes, the elements as As, Cd, Mn, Ni, Pb, Ti and Zn can be found on the particle surface.

Photon-induced X-ray fluorescence (XRF), particle-induced X-ray emission (PIXE), atomic absorption spectrophotometry (AAS) and scanning electron microscopy with X-ray fluorescence (SEM/XRF) are the sensitive methods that are usually used for analysis of contents of suspended atmospheric particles. They all are aimed to determine trace elements, which are connected with difficulties relating to small concentration measurements, each single particle presents complex agglomerate.

Dispersion

Dispersion of the atmospheric particles in the air is affected by meteorological conditions (wind, speed, wind direction and atmospheric stability), the emission height (*e.g*. ground level sources such as road traffic or high level sources such as tall chimneys), local and regional geographical features. Meteorological conditions can be described as either stable or unstable, where the stability is determined by wind (which stirs the air) and heating effects (which cause convection currents).

Atmospheric stability affects pollution released from ground level and elevated sources differently. In unstable conditions, ground level pollution is readily dispersed thereby reducing ground level concentrations. Stable conditions mean less atmospheric mixing and therefore higher concentrations around ground level sources, but better dispersal rates and therefore lower ground level concentrations for elevated plumes.

Importance of Aerosols for Human Health

A series of epidemiologic studies has clearly shown the causative interconnection between particles and health effects: frequency rates of chronic obstructive respiratory diseases seem to be increasing. The World Health Organization (WHO) as well as different authorities in Europe and the US, recognized the potential risks of atmospheric particulate matter, PM to public health, and atmospheric pollution by particles has become an important policy theme.

Air Quality Standards

The Council of the European Union has adopted Directive 1999/30/EC of 22 April 1999 relating to limit values for sulphur dioxide and oxides of nitrogen, particulate matter PM_{10} and lead in ambient air. The limit values for PM_{10} are 50 μgm^{-3} (24 h mean) not to be exceeded more than 35 times per year, and 40 μgm^{-3} as an annual mean; these limits have to be achieved by January 1, 2005. In our country, limit values are still related to total suspended particles and for urban areas daily limit amounts 120 μgm^{-3} and mean annual value is 70 μgm^{-3}.

Air Quality Studies

Sampling of suspended particulate matter, PM_{10} and $PM_{2.5}$ started in July April 2003 and are still in progress at three sites in the very urban area of Mitrovica: roof of the FXM building MIP, roof of the elementary school "Bedri Gjina" at about 4 m height; 40 m far from heavy-traffic streets; on the platforms above entrance stairs to the faculty of Mining at the height above 3 m from the ground Table 2.

Suspended particles were collected on Pure Teflon filters, Whatman (37 mm diameter, 2 µm pore size) and Pure Quartz, Whatman (37 mm diameter) filter paper, using the low volume air sampler Mini-Vol Airmetrics Co, Inc. (5 l min^{-1} flow rate). The duration of each sampling period was 24 hours. The filter samples were sealed in plastic bags and kept in portable refrigerators, in horizontal position during transport back to the laboratory. Particle mass was gravimetrically determined by weighting loaded and unloaded filters, after 48 hours conditioning in a desiccator's, in clean room class at the temperature 20 ˚C and constant relative humidity RH around 50%.

For a quality assurance procedure, the quality of sample collection was determined by collecting blank samples in the field and by three control filters. During the sampling, conventional meteorological parameters were regularly recorded at the Meteorological Station of the Hydro-meteorological Institute of Kosova located inside central urban area.

Results and Discussions

Daily mass concentrations of 105 PM_{10} and 48 $PM_{2.5}$ samples were determined by gravimetric analysis of filters that were exposed to urban air in Mitrovica from April 2003 to April 2005. A seasonal variation was found in autumn-winter period (October, November, and December) which could possibly be attributed to the higher traffic density and combustion of fossil fuels for heating during winters, as well as to the prevailed meteorological conditions, inversed layers, low temperature and stagnation of air masses.

The PM mass concentration levels in Mitrovica urban air and in some European cities are presented in Table 1, showing that our annual mean PM mass concentrations in some others

European cities. The identification of hematite and goethite as the main components in TSP and PM_{10} filters and pellet plant dusts, and their absence from "background" samples strongly indicated that fugitive emissions emanating from the pellet plant were the source of airborne Fe and Pb dusts responsible for ongoing environmental contamination.

Table 1. Annual mean PM mass concentrations (μgm^{-3}) in urban air in Mitrovica and some European cities

	Mitrovica, 2003	Milan, 1998	Madrid, 1999-2000	Roma, 1999	Berlin, 1998	Mitrovica, 2005
PM_{10}	187	103 (W) 68 (S)	48	60	38	183
$PM_{2.5}$	109	66 (W) 43 (S)	34		30	94

The mineralogy of the "background" TSP and PM10 filters exhibited noticeable differences compared to those collected on Mitrovica urban area with wind days "Fig 1". The main differences were:

- The mineralogy of the background filters was simpler than identified for Mitrovica wind sector days, with only 5 minerals (quartz, halite, hematite, calcite and anglesite).
- PM10 filters dominated by halite, which constituted 100% of the mineralogy of all 30 filters.
- Halite also constituted 100% of the TSP filter collected on 2003.
- Goethite, magnetite and kaolin (clay) were absent from all filters.

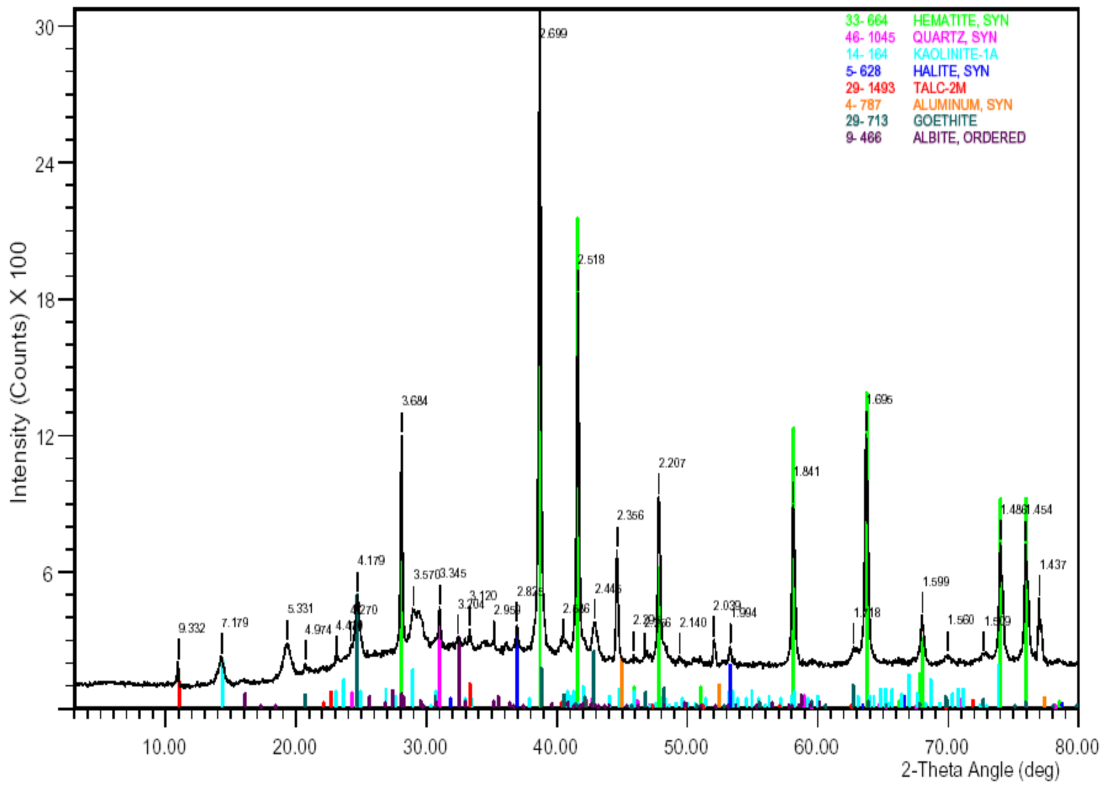

Figure 1. Quantitative X-ray diffraction characterise and quantify the mineralogy of the total suspended particulate (TSP) and particulates <10 µm (PM_{10}) filters.

Table 2. Concentration of heavy metals (Pb, Cd and Zn)

		Annual average concentration, (µm m^{-3})		
Nr.	Monitoring sites	Pb	Cd	Zn
1	Sh.f. "Bedri Gjina"	0.65	0.039	2.31
2	Faculty-FXM	0.62	0.037	1.94
3	Sh.f. "1 Maji"- Shupkovc	0.57	0.021	1.82
4	Bair - Monopoli	0.31	0.009	0.91
5	Sh.f. "Eqrem Çabej"	0.56	0.041	1.22
6	OJQ "Mitrovica"	0.59	0.028	1.38
	Maximal value	0.65	0.041	2.31
	Minimal value	0.31	0.009	0.91

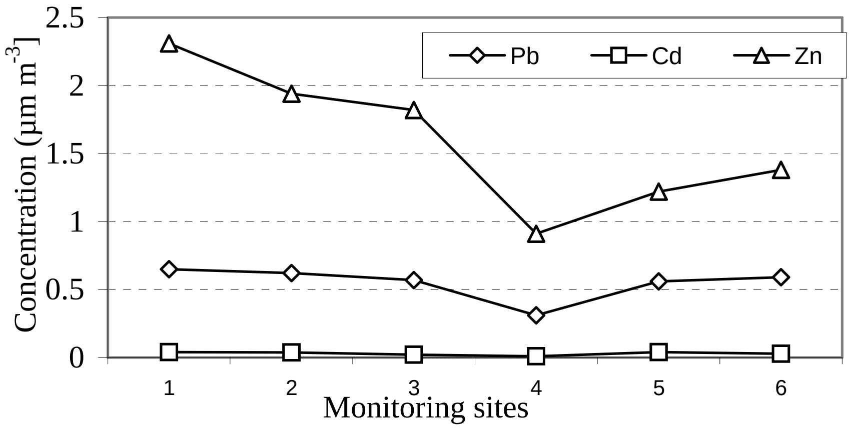

Figure 2. Diagram concentration of heavy metals (Pb, Cd and Zn)

Conclusion

Air quality investigation in Mitrovica urban area has shown that the annual PM mass concentrations, in comparison to majority of European cities are significantly higher. The main sources of suspended particle are traffic, tailings, local heating and dust re-suspension.

Project and investigation are in progress.

The obtained results and further investigations will substantially improve our knowledge in estimating parameters that define transport distribution and interaction of pollutants from the sources of pollution to human population and are aimed for finding effective solutions to improve air quality and for a sustainable development in urban areas.

The overall lead, cadmium and zinc content are found in the PM fraction “Fig 2 and Table 2”. There was significant correlation between lead, cadmium and zinc concentrations. While seasonal trend of lead concentrations is obvious, showing elevated concentrations during autumn-winter period, no such trend for cadmium concentrations could be determined.

Acknowledgment: *Acknowledgements the authors gratefully acknowledge the MESP and WHO for financial support and technical support.*

References

EEA(2003), Air Quality in Europe State and Trends 1990-1999. topic Report 4/2002. European Environment Agency, Copenhagen.

EEC (1999). European Council Directive 1999/30/EC. Official Journal L. 163, 41-60.

EMEP (2002). Manual for sampling and Chemical Analysis.

EN 12341 (1998). Determination of the PM10 fraction of suspended particulate matter, Reference method and field tests procedure to demonstrate reference equivalence of measurement methods.

EN 14907 (2005). Standard gravimetric measurement method for the determination of PM2.5 mass fraction of suspended particulate matter.

J Shwartz, D.W. Dochery, L.M (1996). Is daily mortality associated specifically with fine particles. *Journal, Air waste manages Assoc*. **46**, 927-939.

Syla A., Veliu A. (2005). Air quality monitoring 2000-2005 in Kosova, Prishtina.

Willeke K., Whitby K. T., (1975), *JAPCA* **25**, 529.