HEAVY METALS CONTENT IN PM_{10} SAMPLES AT TWO URBAN ROMANIAN SITES

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ABSTRACT. - Heavy metals content in PM_{10} samples at two urban Romanian sites. Aerosol particles were traditionally investigated in Romania for their metal content in extremely polluted areas (critical polluted areas) like Copsa-Mica or Baia Mare, because of their negative effects on water, soil and vegetation in their surrounding regions. However, combustion of fossil fuels, metal production and waste incineration, main sources of toxic metals such as Cd, Pb, Ni, might be also located nearby of other cities. Therefore, even here the population can be exposed to the potential harmful effects of these toxic metals and the air quality can be seriously affected if high concentrations are attained. Present work assesses concentrations, variability, and compliance with the EU regulations of the trace metals Ni, Cd, Pb levels in PM_{10} samples in two Romanian cities, Iasi and Cluj, at urban background and traffic stations. The cities have a medium size but because of their rapid development both cities play an important regional role. They also present different topographies and different climatic characteristics. Data were extracted from European AQ database AirBase for the period 2009-2012. Measurements of PM_{10} and $PM_{2.5}$ are obtained by gravimetric analysis and those of heavy metals (Pb, Cd, Ni) by atomic absorption spectrometry. Data sets are acquired through measurements made on a daily average basis. Measurement annual and seasonal summary statistics were performed and analyzed for all data during 2009-2012 for Iasi and for 2010 for Cluj.

Keywords: air pollution, air quality standards, particulate matter, heavy metals, Pb, Cd, Ni, East Europe.

1. INTRODUCTION

Air pollution represents the change of air composition with or without the addition of new compounds, harmful to humans, animals, plants or aquatic systems. The study of pollution over years resulted in publications and studies regarding various types of pollution. Studying the evolution of pollution, one can find ways to diminish the effects or can be created alarm signals for protecting the public from polluted area. An important component of the study of pollution is the understanding of the phenomenon, and this can be realized only by studying the pollutants.

A pollutant may be considered safe under a certain concentration, but must be avoided atypical situations when these pollutants can become dangerous even in concentrations considered safe (ex: Great Smog of London, UK, 1952 [1,2]), and outline the developments regarding the impact of pollutant to generate

information useful in the effort to reduce pollution. For Romania, the highest air pollution level is encountered in Bucharest [3]. Particulate matter PM_{10} (particles with diameter less than 10 µm) or $PM_{2.5}$ (particles with diameter less than 2.5 µm) containing heavy metals constitute a class of pollutants with a major impact on the biosphere, dispersed in the air or in the aquatic environment [4]. Due to their complex chemical composition, when particulate matter is removed from the atmosphere by various processes, the depositions of each component chemical species influence both land or aquatic environments at local and regional scale [5].

Our study conducted an analysis of variability of the mass concentration of particulate matter with a diameter less than 10 µm and of their main heavy metals' content (Cd, Pb, Ni), in two cities in Romania, Iasi and Cluj. This study with gives us a first picture of air pollution regarding the heavy metal content of PM_{10} samples in the two cities using an inexpensive computing approach. In terms of monitoring stations, the approach could be expanded when the use of mobile sampling systems would be available.

2. METHODS

2.1. Sampling sites

Table 1 contains information about the two cities on which the study was conducted and Figure 1 shows details of the cities and their surrounding areas.

Table 1. ***Coordinates of sampling sites***

City	Altitude (m)	Geographical coordinates		Surface (km^2)
		Latitude	Longitude	
IASI	200	45°9'44" N	27°35'20" E	94
CLUJ	410	46°46'0" N	23°36'0" E	179.5

Iasi city is the seat of Iasi county and is located in the eastern part of Moldova in an area of hills. The climate in the area of Iasi has a strong continental character which is defined by the hills influence at the ground levels on air masses with eastern origins. This area has as a characteristic high temperatures recorded in summer with associated droughts. The air masses from north and northeast lead to winter blizzards having a high frequency. The average annual temperature is 10-11 °C, July average temperature is 23 °C and in January is -3 °C. The absolute maximum temperature was 40 °C (27 July 1909), and the absolute minimum temperature of -36.3 °C (1 February 1937).

Cluj-Napoca is the seat of the Cluj county, in the heart of Transylvania. It is located between the Apuseni Mountains, Someş Plateau and the Transylvanian Plain and spreads over the valleys of Somesul Mic and Nadas. It is surrounded on three sides by hills with heights between 500 and 825 meters.

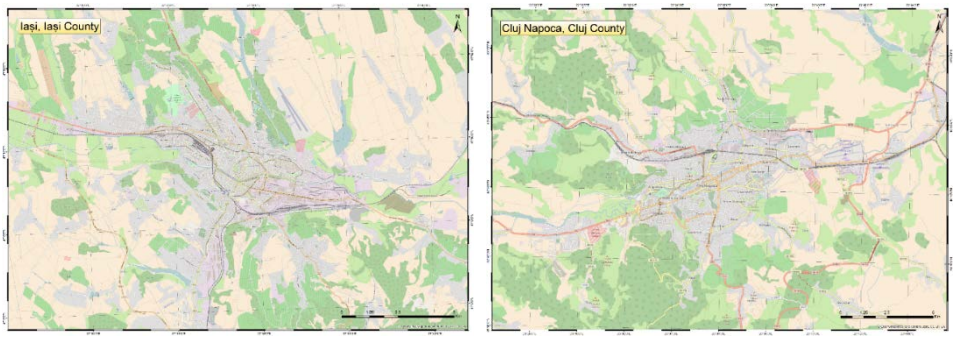


Fig. 1. ***Details of the cities and their surrounding areas*** [2]

The climate of Cluj-Napoca is moderate continental. The proximity of Apuseni Mountains plays an important role in the topoclimate of this region, in the fall and winter influences from the west Atlantic are felt. The average annual air temperature is about 8.2 °C. July average temperature is 19 °C, and in January of -3 °C. The absolute minimum temperature was -34.5 °C (January 1963), and the absolute maximum temperature of 38.5 °C (August 1952).

2.2. Data, sampling methodology and analysis

Data were extracted from European AQ database AirBase for years: 2009, 2011 and 2012 for traffic and urban background stations in Iasi and Cluj [6].

The traffic type station monitors traffic influence on air quality. Radius of monitoring area varies between 10-100 meters. The monitored pollutants are: sulfur dioxide, nitrogen oxides, carbon monoxide, PM_{10}, $PM_{2.5}$, lead and volatile organic compounds: benzene, aldehydes and main organic compounds – aromatic hydrocarbons (COV). The urban stations monitor the influence of urban and suburban settlements over air quality. Radius of monitoring area varies between 1 and 5 km. Both types of stations monitors the same pollutants along with other meteorological parameters (wind direction and speed, temperature, precipitations, pressure, humidity and solar radiation).

Measurements of PM_{10} and $PM_{2.5}$ were performed by gravimetric analysis and those of heavy metals (Pb, Cd, Ni), in PM_{10}, by atomic absorption spectrometry. Data sets are acquired through measurements made on a daily average basis. Annual and seasonal summary statistics were performed through analyzing all data acquired during 2009, 2011 and 2012 for Iasi and in Cluj for 2010 because the available data are limited to this year.

There were investigated the levels of mass concentrations of PM_{10} and de heavy metals contained in: Ni, Cd, Pb. The study was aimed at identifying the minimum, maximum and average values. The median values were calculated in order to characterize the average of the pollution state. The standard deviation will give us a measure of the natural variability of the concentrations of particulate matter and heavy metals for the chosen time periods. In order to check for the existence of the normal distribution of the observations, skewness and kurtosis parameters were calculated as well.

3. RESULTS AND DISCUSSION

The annual statistics for PM_{10}, Cd, Ni, Pb is presented in Table 2 for Iaşi (traffic station) and in Table 3 for Cluj (traffic and urban background stations). The observations follow a normal distribution in a very good approximation as the statistical parameters skew and kurt indicate.

Table 2. ***Annual statistics for Iasi, traffic station***

Year	Pollutant	MIN	MAX	MEAN	MED	SD	SKEW	KURT
2009	Cd (ng/m³)	0.03	4340.0	69.96	0.26	319.22	0.75	7.81
	Ni (ng/m³)	0.00	11.40	1.59	1.41	0.67	0.97	7.74
	Pb (µg/m³)	0.01	0.09	0.02	0.02	0.01	-1.26	0.79
	PM_{10} (µg/m³)	11.96	179.5	48.99	41.08	9.31	-0.09	0.65
2011	Cd (ng/m³)	0.09	3280.0	519.20	0.65	294.55	0.51	3.91
	Ni (ng/m³)	0.01	17.49	2.78	1.85	0.89	0.62	2.26
	Pb (µg/m³)	0.01	0.04	0.02	0.02	0.0	-0.15	-1.0
	PM_{10} (µg/m³)	7.04	144.25	43.40	41.07	7.77	0.31	-1.64
2012	Cd (ng/m³)	0.06	2420.0	290.85	0.59	333.44	0.16	9.14
	Ni (ng/m³)	0.02	6.38	2.64	2.66	0.20	-0.31	-0.48
	Pb (µg/m³)	0.01	0.15	0.04	0.03	0.01	0.99	-1.55
	PM_{10} (µg/m³)	3.18	165.47	47.51	45.30	11.34	-0.11	-0.87

med= median; sd= standard deviation

Table 3. ***Annual statistics for heavy metals at Cluj, traffic and urban background station***

Year	Station	Pollutant	MIN	MAX	MEAN	MED	SD	SKEW	KURT
2010	Traffic	Cd (ng/m³)	0.0	15.90	1.37	0.44	1.36	0.06	0.34
	Urban	Cd (ng/m³)	0.0	7.45	0.63	0.22	0.50	-1.31	4.55
	Traffic	Ni (ng/m³)	0.0	3.71	0.65	0.46	0.26	-0.55	2.21
	Urban	Ni (ng/m³)	0.0	3.74	0.44	0.25	0.26	-1.78	-1.57
	Traffic	Pb (µg/ m³)	0.0	0.03	0.01	0.01	0.0	n.a.	4.59
	Urban	Pb (µg/ m³)	0.0	0.03	0.01	0.01	0.0	n.a.	n.a.
	Traffic	PM_{10} (µg/m³)	0.0	114.59	33.61	33.54	3.78	0.97	2.33
	Urban	PM_{10} (µg/m³)	0.0	108.06	29.39	24.89	5.70	0.71	3.10

n.a. = not available; med= median; sd= standard deviation

Measured ambient annual (average and median) heavy metal concentrations have the highest values at Iasi urban site in comparison with Cluj at both traffic and

urban background sites. However, for both cities, among all metals, cadmium mass concentrations show significant higher values during all years.

Mass concentrations range of particulate matter and metals Cd and Ni in Iasi and Cluj present significant variations between the cities, whereas Pb levels show the lowest variations at both annual and seasonal scales.

High levels of PM_{10} mass concentrations in Iasi and Cluj were first revealed in reference [7] where the annual and seasonal temporal trends of PM_{10} and $PM_{2.5}$ for Iasi and Cluj, together with other urban and rural sampling sites in Romania were also reported. Our results for PM_{10} fit within those in reference [7].

Figure 2 and Figure 3 illustrate the average seasonal variation of cadmium and PM_{10} mass concentrations for Iasi (for the years when the highest levels were registered) and, respectively Cluj. As shown in the figure 2, Cd seasonal concentrations in Iasi lie within the range of 72.40 ng/m^3 (winter) and 801.00 ng/m^3 (summer). On the contrary, for Cluj, cadmium concentration varies between 0.28 ng/m^3 (summer) and 2.78 ng/m^3 (winter). We also show here (Figure 3) that PM_{10} concentrations reach their highest levels in spring and are almost equally distributed in the rest of the seasons in Iasi. Cluj presents a different pattern, with a lower seasonality of PM_{10} levels than Iasi, with a minimum in summer (about 26 µm/m^3) and a maximum in winter (about 40 µm/m^3), which is a typical pattern in urban areas.

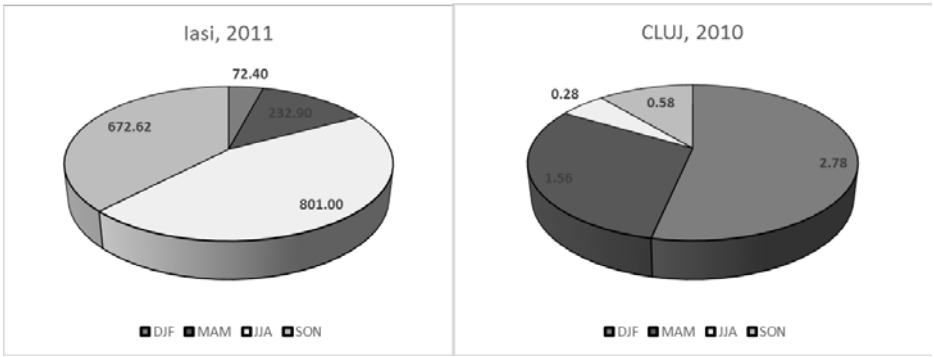
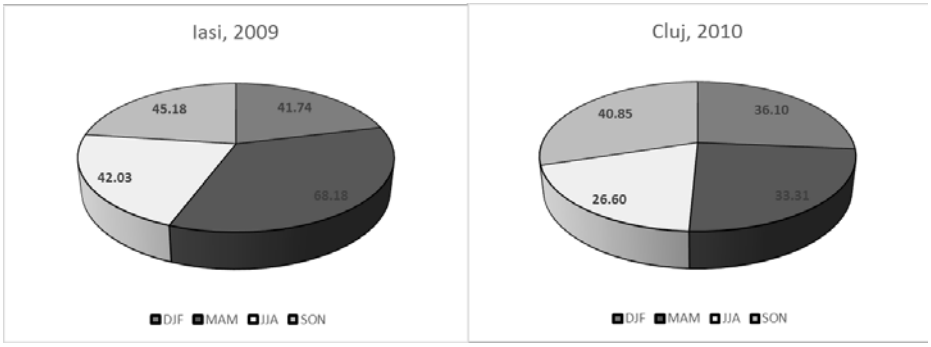


Fig. 2. ***Seasonal averages for Cadmium in Iasi and Cluj for traffic stations***



DJF= winter, MAM= spring, JJA= summer, SON= fall

Fig. 3. ***Seasonal averages for PM_{10} in Iasi and Cluj for traffic stations***

Table 4. ***Number of exceedance of the limit values for each pollutant; EU limit values are also indicated***

IASI				CLUJ			
Year	**Station**	**Pollutant**	**Nr. of exceedance**	**Year**	**Station**	**Pollutant**	**Nr. of exceedance**
2009	**Traffic**	**Cd (ng/m³)**	12	**2010**	**Traffic**	**Cd (ng/m³)**	16
		Ni (ng/m³)	0		**Urban**	**Cd (ng/m³)**	2
		Pb (µg/m³)	0		**Traffic**	**Ni (ng/m³)**	0
		PM_{10} (µg/m³)	88		**Urban**	**Ni (ng/m³)**	0
2011		**Cd (ng/m³)**	103		**Traffic**	**Pb (µg/ m³)**	0
		Ni (ng/m³)	0		**Urban**	**Pb (µg/ m³)**	0
		Pb (µg/m³)	0		**Traffic**	**PM_{10} (µg/ m³)**	31
		PM_{10} (µg/m³)	38		**Urban**	**PM10 (µg/ m³)**	26
2012		**Cd (ng/m³)**	69	**Limit values**		**Cd (ng/m³)**	**5**
		Ni (ng/m³)	0			**Ni (ng/m³)**	**20**
		Pb (µg/m³)	0			**Pb (µg/m³)**	**0.5**
		PM_{10} (µg/m³)	62			**PM_{10} (µg/m³)**	**50**

The number of exceedances observed in the present study are comparable with those observed in the capital of the country in 2010 [3], when for Bucharest traffic sites the following numbers of exceedances were registered: 87 at a wide street sampling site and 57 at a canyon street sampling site.

4. CONCLUSION

This study contributes to the knowledge on air pollution in East Europe, presenting an assessment of the ground-level concentrations of heavy metals in PM_{10} in two urban Romanian cities. Ambient metal pollution levels, their variability and exceedances are discussed in the context of air quality status in both cities.

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