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POLLUTION WITH PARTICULATE MATTER IN A FORMER METALLURGICAL CENTER OF ROMANIA (CĂLAN)

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SUMMARY

Fine particulate matter is a complex mixture of very small particles and liquid droplets that can be very harmful to health. Atmospheric particles inhaled through the respiratory tract can be very harmful. Large particles are retained in the nasal cavity and pharynx, while the small particles reach the lungs and are retained there, the respiratory system it has a mechanism for the elimination of the inhaled particles. In this paper we proposed to follow the evolution of the ambient air quality in terms of emissions of heavy metals (Pb, Ni, Cd) and particulate matter (PM_{10}) in the area of the old steel mill from Călan City.

Keywords: particulate matter; PM_{10}; $PM_{2.5}$; heavy metals; lead.

INTRODUCTION

Particulate matter (PM) is one of the most common air pollution entities and is known to have significant impacts on the environment and human health. Particulate matter, in most basic terms, refers to a complex mixture of solid particles and liquid droplets found in ambient air. Particle pollution includes inhalable coarse particles, fine particles and ultra-fine particles.

Coarse particles are generally defined as those having an aerodynamic diameter larger than 2.5 μm ($PM_{2.5}$) and smaller than 10 μm aerodynamic diameter (PM_{10}). Fine

particles are those having an aerodynamic diameter less than 2.5 μm, and ultra-fine particles are those, less than 100 μm in diameter. While particulate matter is produced from diverse sources via different formation mechanisms and may be composed of numerous chemical compounds, it can be generically categorized as consisting of either primary or secondary particles [1].

Primary particles are emitted directly from sources such as combustion exhaust systems and stacks, fires, sea sprays, construction sites and unpaved roads. Secondary particles form in the atmosphere through the reaction of numerous compounds, such as sulphur dioxide (SO_2) and nitrogen oxides (NO_x) released from the combustion of fossil fuels, and various volatile organic compounds [2].

Secondary particles make up most of urban air pollution and are strongly linked with adverse health effects, including cardiovascular and pulmonary ailments and premature deaths in people with heart or lung decease. Moreover, secondary particles mostly contain fine and ultra-fine particles that are more easily inhaled, compared to larger particles, deep into the lungs. These very fine particles contain higher concentrations of acidic species of sulphur and nitrogen compounds than larger particles, enforcing the hypothesis that lung and heart ailments are more closely associated with fine and ultra-fine particles [3].

Particle size is directly related to the potential to cause effects. An important issue is the particles with aerodynamic diameter less than 10 μm, which pass through the nose and throat and penetrate the alveoli causing pulmonary inflammation and intoxications. Are especially affected people with cardiovascular and respiratory diseases, children, elderly and asthmatic people.

Children younger than 15 years inhale more air and therefore more pollutants. They breathe faster than adults and tend to breathe more through their mouth, bypassing the natural filter, nose. They are particularly vulnerable because their lungs are not completely developed, and lung tissue that develops in childhood is more sensitive. Dust pollution worsens asthma symptoms, producing cough, chest pain and breathing difficulties. Long-term exposure to low concentrations of dust can cause cancer and premature death [4].

Atmospheric particulate matter (PM) and its impact on public health, the global climate and on visibility have been longstanding concerns of the air quality management community and regulatory authorities. Understanding the adverse effects of particles and devising appropriate control strategies requires spatial and temporal information on PM mass concentration, aerodynamic size and chemical composition. Several epidemiological studies have observed negative health effects related primarily to enhanced levels of fine particles with an aerodynamic diameter less than or equal to 2.5 μm ($PM_{2.5}$) [5].

The U.S. National Ambient Air Quality Standard (NAAQS) daily standard for $PM_{2.5}$, was lowered from 65 $\mu g \cdot m^{-3}$ to 35 $\mu g \cdot m^{-3}$, but the 15 $\mu g \cdot m^{-3}$ annual mean was

left unchanged. The European Union has recently adopted a new $PM_{2.5}$ Standard of 2.5 μg• m^{-3} annual mean (based on 3-year average) with target attainment by 2015 [6].

Romania has a national network of air quality monitoring and in each county Environmental Protection Agencies are required to monitor air quality in cities, placing as many points of air sampling as is necessary and in rural areas where it must be placed a measuring center located at each 100,000 km^2 as required by law and by posting the data obtained from monitoring air quality.

The study follows the evolution of pollution with particulate matter and heavy metals in a metallurgical center of reference from Romania, Călan city. The city is located in the central region of Romania (Haţegului Country) and it is positioned at 28 km from Deva - Hunedoara county residence. The city is situated at an altitude of 230 m with an area of 101.5 km^2.

Between 1869 and 1871 were put into operation two blast furnaces which were using dolomite and ore from their own mines from Teliuc. The plant, named Victoria-Călan, turn cast iron into steel in a unit with a capacity of 4,000 tons steel/year. During the communist regime, the plant was growing very much, turning it into a steel mill. Victoria-Călan plant was the largest producer of cast iron in the country, at the same time, the main supplier of steel ingot molds and plants accessories for the metallurgical plants of Hunedoara and Reşiţa.

Unfortunately, after 1989, the mill disintegrates piece by piece by multiple causes leading today to about 250-300 workers employed most of them for guarding.

As sources of pollution of the area, in present we can mention in addition to large quantities of powder coke from the old steel mill, railway traffic, the railway crosses the old steel mill, the traffic from Route 66 that runs through the old town Călan, the gas station and the 3 ballasts which are using as raw material, among other things, the concrete came from the former steel mill buildings, all built on the site of the steel mill.

The rail traffic, road traffic and the gas station are sources of particulate matter pollution (PM_{10} and $PM_{2.5}$) and major sources of lead, one of the most dangerous pollutants for human health because it is carcinogenic and the ballasts are a source of dust and particulate matter.

We also remember the main dumps and ponds as a feature of Hunedoara county, whose particles are driven by the wind over distances of tens of kilometers. Mineral powders contained in the combustion gases discharged into the atmosphere, especially when gas cleaning installations are malfunctioning or are not working at all, is a serious threat for the plants, soil and air. By submitting on soil and plants due to their own sedimentation or due the precipitation action, it leads to an increase in the concentration of heavy metals.

MATERIALS AND METHODS

In Hunedoara county there are 6 air quality monitoring stations, the 4th station is located in the town of Călan. Station HD4 - industrial background, from Călan (Furnalistului Street) is located in the old Victoria Călan steel mill and being an industrial type station has the following characteristics:

- evaluate the influence of industrial activities on air quality;
- radius area of representativeness is 100 m - 1 km;
- pollutants monitored are sulfur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide (CO), ozone (O_3), volatile organic compounds (VOCs), particulate matter (PM_{10} and $PM_{2.5}$);

Methods of analysis

a) Determination of particulate matter is made according to STAS 10813-76 [7].

The method consists in the aspiration of a volume of air on membrane filters with average pore size of 0.80 to 0.85 μm and weighing of powders deposited on the filter.

Sampling is done by vacuuming the air at a rate of 15 ÷ 40 L/minute (21.6 to 57.6 m^3/day). The difference between the mass filter after exposure and the mass filter before the exposure represents the total amount of particulate matter in the sample.

The content of particulate matter is calculated using the relationship:

$PM = (m_1 - m_2) / V, [\mu g/m^3]$

where: m_1 = filter mass after exposure, in μg; m_2 = filter mass before exposure, in μg
V = volume of air sucked, in m^3.

b) Determination of Pb, Cd and Ni in the PM_{10} fraction of suspended particles is made according to EN 14902:2007 [8]. Samples containing Pb, Cd, As can be accomplished using a PM_{10} sampler. In general, the sampling time should be 24 hours.

The filter is transported in the laboratory and Pb, Cd, Ni and As are placed in solution in a closed vessel (microwave) using nitric acid and hydrogen peroxide. The solution which results is analyzed by atomic absorption spectrometry with graphite furnace (GFAAS) or mass spectrometry with inductively coupled plasma (ICPMS).

The mass m_a of the analyte "a" from the filter, in μg, is calculated using the following equation:

$m_a = B_a \times V_s \times F \times A_{tot}/A_{part}$

where: m_a = analyte "a" collected mass, in μg

B_a = mass concentration of analyte "a" in the sample solution, in μg/mL

V_s = sample solution volume, in mL; F = dilution factor (F = 1 when the sample solution is not diluted); A_{tot} = exposed filter surface, in cm^2; A_{part} = mineralized surface area of the filter, in cm^2.

RESULTS

After collecting and analyzing samples for 2009 and 2010 were obtained the following results (Figure 1 and Figure 2):

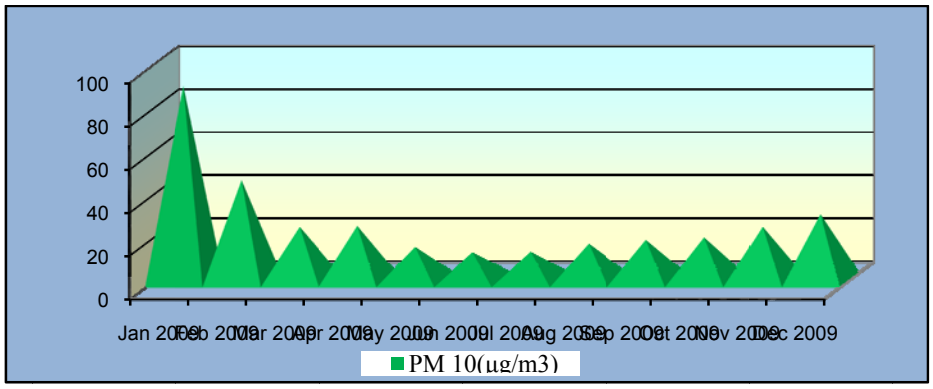

Figure 1. Monthly evolution of PM_{10} concentrations ($\mu g/m^3$), in 2009

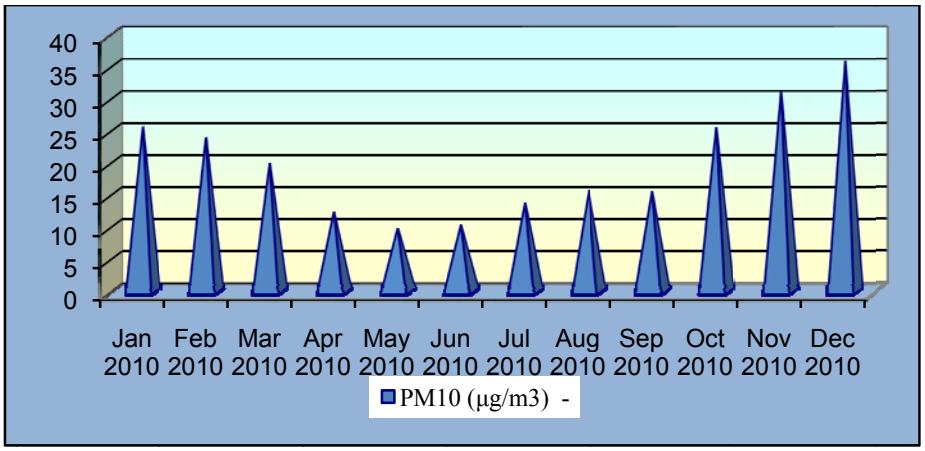

Figure 2. Monthly evolution of PM_{10} concentrations ($\mu g/m^3$), in 2010

The values in autumn-winter months (from October, November, December, January, February) are higher than in the other months. The same trend is observed in 2010 but, the recorded values are much smaller (maximum of 35 µg/m^3 against 83 µg/m^3 in the previous year) compared to previous years (Figure 3)

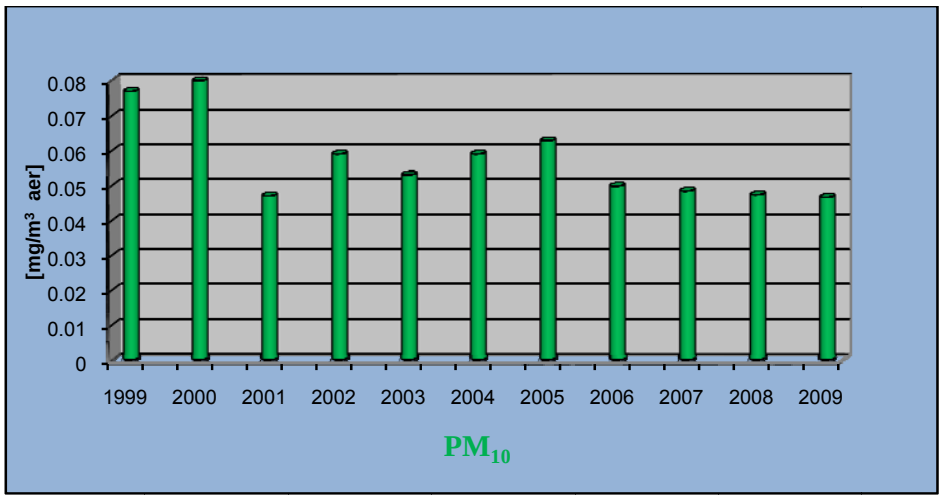

Figure 3. Evolution of PM_{10} concentrations (µg/m^3, averages), between 1999 and 2009

Heavy metals (lead, cadmium, nickel, etc.) are compounds that cannot be degraded naturally, having a long residence time in the medium, in long term are dangerous because they can accumulate in the food chain. Heavy metals can cause muscle disorders, nervous, digestive disorders, can induce a general state of apathy; may affect the development of plants, preventing the normal course of photosynthesis, respiration and perspiration.

Lead is among the heavy metals most often monitored, due to its high toxicity. During 2009 (Figure 4) stands a maximum in spring and summer months, while in 2010 (Figure 5) minimum values are found in the summer months.

Higher concentrations of Pb in 2010 compared to 2009 can be attributed to the upgrading of Route 66 that took place during the entire summer, the emissions from the modernization machineryes have contributed greatly to increasing the concentrations of Pb and particles in suspension.

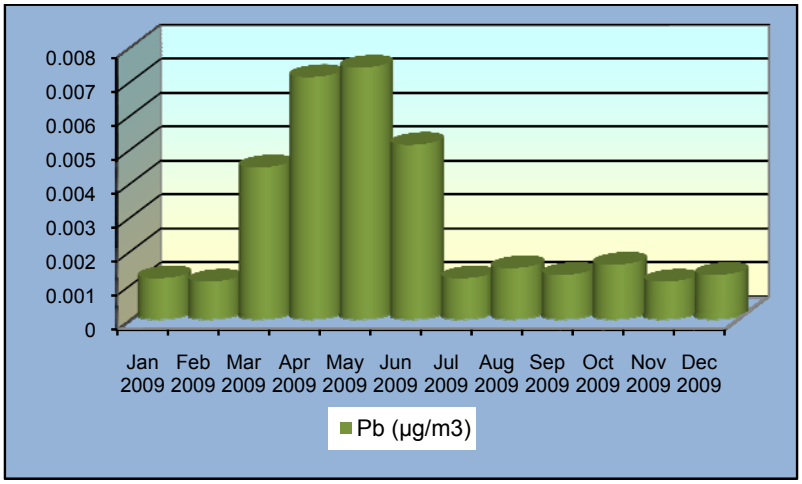

Figure 4. Monthly evolution of Pb concentrations (µg/m^3), in 2009

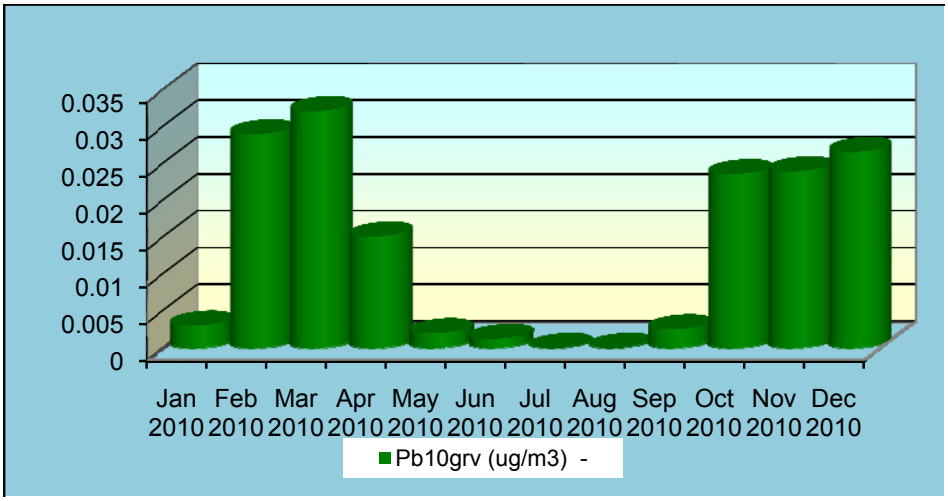

Figure 5. Monthly evolution of Pb concentrations (µg/m^3) in 2010

Compared to lead, cadmium and nickel were found in much higher concentrations in particulate matter (Figure 6) between the months February to April.

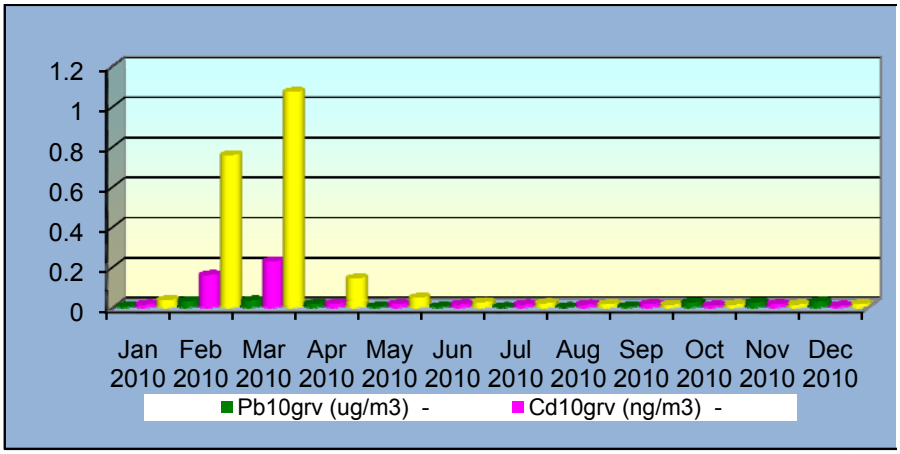

Figure 6. Comparison between monthly evolution of heavy metals (Pb, Cd, Ni), in 2010

DISCUSSION

As can be seen from figure 1, during 2009, higher values of PM_{10} concentrations were recorded especially in the winter months, and keeping the trend during 2010 (figure 2). Higher values of this period is mainly due to the use of wood as a source of heating the homes, in the area there are approximately 250-300 homes using wood stoves for heating during the winter season. Thus, the products resulting from burning are a major source of PM_{10}. Lack of winter rains also contributes to maintaining a high concentration of suspended particles.

During the summer, the concentration of PM_{10} decreases, once the heat has come, high temperatures during this period contributes to the destruction of particulate matter and heavy rains that wash the dust and particles, are transporting them into soil, thereby reducing their concentration in the air.

Average daily concentrations of particulate matter under 10 microns (PM_{10}) in ambient air, obtained gravimetrically, did not exceed over 35 times (number of exceedances allowed) in 2010, the daily limit (50 $\mu g/m^3$/24h) provided for human health in Order MAPM 592/2002. Were recorded daily average concentrations above the limit of 50 $\mu g/m^3$/24 h, but not exceeding the maximum allowed.

Figure 3 presents the average concentrations of PM_{10} in the last 10 years, a trend which is oscillatory, with the general trend of decreasing concentrations of particulate matter, especially in the last four years.

During the years 2009 and 2010 were made determinations of lead, cadmium and nickel in particulate matter (PM_{10}) from gravimetric analysis of filters collected from air quality monitoring station HD 4 - Călan. The limit value for PM10 measurements of lead, provided the Order MAPM no. 592/2002 of 0.5 $\mu g/m^3$/year, was not passed in 2009.

Lead emissions have decreased by 65.2% towards last year (2008); this decline was caused largely by the fact that in 2009 has not been used in transport leaded petrol.

Regarding to cadmium (figure 6), Order M.M.G.A. no. 448/2007 provides for annual average concentrations of cadmium measured in PM10 fraction a target value equal to 5 $\mu g/m^3$. Annual value registered for cadmium, from the fraction of PM10 was 1.418 $\mu g/m^3$.

The annual value registered for nickel (figure 6), from the fraction of PM_{10} was 1.293 $\mu g/m^3$ at HD-4 Călan station, value that has not exceeded the target set out in M.M.G.A. Order no. 448/2007 of 20 $\mu g/m^3$.

CONCLUSION

Air quality in the Călan city continues the overall trend to improve in the last years. The level of contamination of the atmosphere presents a decrease for the indicators: particulate matter (PM_{10}) and heavy metals compared to previous years, according to data obtained from air quality monitoring network.

Following the determinations made over the suspended particles (PM_{10}) we establish a general trend of decreasing concentration of these particles, especially in summer and in the winter a slightly higher concentration, but has not exceeded the annual limit allowed for human health.

Regarding on heavy metals from particulate matter, the observations we made shows also a tendency of decreasing of their concentrations, in recent years, especially in summer, concentrations decreased to almost zero due to largely exclude the use of gasoline lead.

Ambient air pollution should be a priority today because of air quality we breathe depends on the very quality of life, the polluted air, loaded with dust and other substances is a stressor for people and not only, the plants, the animals, the whole environment has suffered from a polluted air.

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