Comparative Study Regarding Heavy Metals Content in Air from Targu Jiu and Rovinari

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Environmental pollution represents an important and complex subject with a huge concern for both scientists in different fields, but also for the governments, national and international organizations. Besides the indisputable advantages of the industry for the human development, it has a big contribution to environmental pollution with negative effects to the human health. Heavy metals in the environment have negative effects to the ecosystems and to human health. Consequently, it is necessary to determine the level of heavy metals in the environment to take measures to reduce the environment pollution. According to this issue, the main purpose of these research studies is to perform a comparative analysis of heavy metals content in Targu-Jiu and Rovinari area, those being ones of the most pollution affected areas in Jiu county. The results obtained show that the heavy metals contents in PM_{10} in the air in these areas chosen for the study are below the permitted limit values for the period 2015-2016.

Keywords: heavy metals content in air, air quality, PM_{10}

One of the most approached environmental problems is atmospheric pollution due to the complexity and instability of this environmental factor [1-5]. Generally speaking, there is a regional pollution that involves the removal of liquid, solid or gaseous substances in the atmosphere that endanger the human's, plant's and animal's health, may attack materials, reduce visibility, or cause disagreeable odors [6]. On a global scale, the elimination or the accumulation of certain substances in the atmosphere leads to irreparable consequences on the planet's natural balance: the destruction of the ozone layer and the global warming of the atmosphere [7-10]. The results are already visible: on one hand, Earth's surface is constantly subjected to ultraviolet radiation that is not sufficiently filtered by the ozone layer and which is extremely damaging to life, and, on the other hand, warming of the atmosphere produces important climate change [11, 12].

Pollution by heavy metals is of particular concern in urban areas because of high population density, and a great number of pollution sources such as: transport system, industrial plants, domestic waste, corrosion of roadway surfaces [13]. In industry, extractive, steel and metallurgy sector contribute significantly to the pollution of heavy metals and their oxides.

In the metallurgical industry, the production of metals is made from the ores found in nature. The technology of producing these metals first involves concentrating into useful components by removing non-useable components (tailings). This operation is carried out by mechanical processes (flushing or flotation) or by pyrometallurgical processes (roasting). After concentrating, depending on the nature of the metals, the concentrate undergoes a carbon reduction or air oxidation, when metals have been converted to oxides, and sulfur in SO_2. Metal-containing vapors that form with air an aerosol that spreads over long distances from sources have been emitted during these technological operations. They contaminate the environment especially with lead, copper, zinc, nickel, cadmium.

Along with these industrial sectors, combustion of coal for industrial, domestic or electricity generation is an important source of pollution. Pollution produced by the combustion of fossil fuels is closely correlated with their composition. After complete combustion, the resulting polluting dusts are mainly made of ash. The ash in the highest rank coal is found in the proportion of 5-10% and in the lowest rank coal is 40-50% and it is, moreover, one of the quantitative criteria for assessing the quality of coal. The higher the ash content has as effect the lower the calorific value, and consequently the amount of coal consumed for the same purpose becomes higher. From an incomplete combustion of coal, the resulting gases are rich in ash, smoke and unburnt coal particles. Fly ash, eliminated through the smoke chimney of combustion plants, fine ash dust carried by wind from the ash storage pits and charcoal dust from the coal dumps are solid pollutans, which are also found in the form of aerosols.

Environmental waste incineration and the use of fertilizers, especially phosphates can contribute to heavy metals pollution.

When metals come into the atmosphere, they can be an important source of soil, water and plants contamination through the atmospheric deposition phenomenon. Metallic transport of metals depends on their chemical properties - volatile metalloids can be transported in gaseous form or enriched particles (selenium, mercury, arsenic) while other metals are transported in the state of particles (cadmium, lead, zinc) and they can travel very long before depositing on the ground.

Metals, as components of airborne particles, have been the subject of many studies and research into their effects on the environment and human health. This growing concern about environmental pollution with heavy metals is also determined by the phenomenon of their accumulation, especially in areas directly affected by emissions [14-16].

The assessment of the toxicity of metals as a constituent part of PM in the air was carried out under both occupational exposure and *in vitro* and *in vivo* toxicology studies using ROFA-PM (carbon particles which are residual elements from the burning of the perol) or ions soluble metals. In this way, new information was sought on the health effects of PM associated with soluble metals. The metals that can

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be considered as main components of PM are: iron, vanadium, copper, nickel, chromium, cadmium and arsene. They come mainly from anthropogenic sources of fossil fuel burning.

A common feature of heavy metals, whether they are biologically essential (Cu, Zn, Mn, etc.) or not (Cd, Pb, Hg, As), is that they are highly phytotoxic. Pollution causes inhibition of growth, which can become extremely toxic to the cells, ultimately causing the death of plants [17].

Heavy metals can reach the human body by breathing, by ingesting food and water or other liquids, and even by skin.The effects that they produce on the human body depend on their nature, the chemical form under which it penetrates the body, the way of penetration, and the dose. Some of the heavy metals once in the body locate and accumulate in certain organs or tissues, producing chronic or acute intoxication.

Lead-intoxications and its compounds have more effects on the human body. Symptoms of acute lead poisoning are manifested by anoxia, intestinal cramps, vomiting, seizures, and in chronic poisoning, anemia, fatigue, loss of appetite, and finally limb paralysis occur. Exposure to high concentrations of lead causes renal and neurological damages (encephalopathies and seizures). After penetration into the human body, lead is retained in the kidneys and liver, and then stored in the bone where it replaces the calcium. Lead removal from the body takes place at a very slow pace and occurs through urine, bile and feces.

As in case of lead, mercury poisoning can be acute or chronic, the toxic effects depending on the chemical form under which mercury is found and the pathway of penetration into the body. Acute poisoning with organic mercury is manifested by pharyngitis, gastroenteritis, vomiting, nephritis, hemorrhagic ulcerative colitis, hepatitis and circulatory collapse. Chronic mercury poisoning occurs especially in long-term exposure at low concentrations, most often with people working in a specific environment. For humans,the most dangerous are organo-mercury derivatives (methyl-mercury), which cause irreversible neurological damages and even death in the event of ingestion of increased concentrations of mercury.

Another metal element with toxic effects on the human body is cadmium. Toxicology studies have demonstrated the extremely toxic nature of cadmium. Once it enters the body with food, water or breath, it accumulates in the kidneys and in smaller amounts in the liver or other in organs. Accumulation in organs by the use of low-cadmium foods associated with very long elimination periods can lead to severe forms of cadmium poisoning. Cadmium enters in the body via the digestive or respiratory tract, and passes into the circular system by binding to hemoglobin. Symptoms of cadmium intoxication include nausea, vomiting, stomach burns, chills, headaches, and in some cases severe death by cardiovascular collapse and resuscitation paralysis. In the bones, cadmium prevents the deposition of calcium, making it soft, thus inducing spontaneous fractures.

Under these circumstances, most industrialized countries have issued in the last few decades certain regulations on the maximum allowable levels of air pollution. Thus, there is a very intense concern for improving the existing filtering means or for finding new, more efficient and less costly solutions. To achieve more successful improvement of the ambient air quality, the Directive 2008/50/EC on 'Ambient Air Quality and Cleaner Air for Europe' was adopted by the European Parliament and the European Council. It has as the main purpose to inform the public and enterprises about a negative effect of pollution on plantsanimals, humans, and as well as about the necessity for monitoring air pollutants not only at the continuous monitoring stations, but also by using indicator methods, i.e. by analyzing natural deposit media [18].

In areas affected by heavy metals pollution numerous indicators such as pollution indices, integrated pollution index, daily dose average, enrichment factor, hazard quotient, and hazard index have to be analyzed to estimate their effect on the environment and human health [19,24].

In the area of Rovinari and Targu-Jiu there are several sources of pollution that contribute to polluting the atmosphere with various pollutants. Of these, the thermoelectric power plant is the main source of air pollution with various gases (SO_2, NO_x, CO), particulates, heavy metals, various halogen compounds, resulting from the burning of fossil fuels for the purpose of producing electricity. They can also contribute to pollution of the atmosphere, especially with particulates, slag and ash deposits, excavation, dumping, charging and transport of quarries in the immediate vicinity of Rovinari, road traffic and other anthropic activities.

Thus, the main purpose of this research paper is to assess the heavy metals content of PM_{10} fraction in air of Rovinari and Targu-Jiu in order to establish the air quality in the areas selected related to heavy metals content.

Experimental part

Air quality in Targu Jiu is monitored with an automatic air quality station located in the north-west part of the city. In case of Rovinari, the automatic station for air quality monitoring is located in the south-east part. These stations are of industrial type and they have automatic analyzers for the measurement of sulfur dioxide, nitrogen oxides, carbon monoxide and ozone concentrations, and for particulate matter it has an absorption device for collecting particulate PM_{10}on filters for determination by gravimetric method [2]. The concentrations of heavy metals (Pb, Cd, As, Ni) for the years 2015 and 2016 are determined from the dust collected on the filters. The technical failures at the air quality monitoring station made the data capture at the level of the two years of study to be 48.5% in 2015 and 29% in 2016.

The reference method for the sampling and measurement of the PM_{10} fraction is depicted in the European Norm EN 1234l/1999 [20]. The European Norm EN 12341/1999 specifies the performances of the sampling instruments for the PM_{10} fraction in view of the harmonizing of measurements systems, according to the provisions of the Directives of the European Union Council 96/62/EC for the evaluation and management of the environmental air quality [2, 20].

The measuring principle is based on collecting of the PM_{10} fraction separated from the air-floated particles on filters and its gravimetric determination. Filters before and after sampling were conditioned for 24 h by drying, after that they were weighted using an electronic balance with a precision of 10^{-5} g, and they were kept in a clean environment with constant temperature and humidity [2]. The difference between mass of filters after exposure prior to exposure is the amount of particulate matter (PM_{10}) collected [2].

The method used to determine the level of these heavy metals was according to SR EN 14902/2007. Ambient air quality: Standard method for the determination of Pb, Cd, As and Ni in the PM_{10} fraction of suspended particles [21].

The filters that retained particulate matter (PM_{10}) were mineralized using a digester. Mineralization is carried out using hydrogen peroxide and nitric acid.

Mass of each element analyzed from filters is calculated using the equation [2]:

$$m_a = \beta_a \times V_s \times F \times \frac{A_{tot}}{A_{part}} \quad (1)$$

where:

m_a = mass of the element analyzed, in ng;

β_a = concentrationof elementin the sample solution, in ng/mL;

V_s = volume ofsample solution, in mL,

F^s = dilution factor

A_{tot} = surface of filter exposed, in cm^2;

A_{part} = disaggregated surface of the filter, in cm^2 (in this case$A_{tot} = A_{part}$).

The equation number (1) becomes:

$$m_a = \beta_a \times V_s \times F \quad (2)$$

The same procedure was also followed for the control samples.

The concentration of each element in the air sampled, in ng/$m^3$was calculated using the following equation:

$$C_a = \frac{m_a - \overline{m}_{La}}{V} \quad (3)$$

where: C_a = concentration of element in air samples, in ng/m^3;

m_a = mass of element collected on filter, in ng;

m_{La} = the average value of control filter from laboratory, in ng;

V = volume of air sampled, in m^3.

According to SR EN 14902, the concentrations are related to environmental conditions (sampling conditions).For heavy metals analyzed the admissible limit values are considered as annual averages.Interpretation of the results obtained was done in accordance with Law 104/2011 on ambient air quality [22, 23]. Data on heavy metal measurements in air have been requested and obtained from the Environmental Protection Agency Targu Jiu.

Results and discussions

If in 2015 there was a close capture of data for the two areas (51% Targu Jiu and 49% Rovinari), in 2016 the number of measurements represented 86% for Targu Jiu and only 29% for Rovinari of the total days.

However, based on the data obtained from the measurements, a comparative analysis of the degree of heavy air pollution of the air in the two areas can be made.

A first finding, and most importantly, was that after the measurements performed there were no values that were above the limits allowed for the elements analyzed in the two areas.

For lead, the annual mean concentrations over the two years of study showed slightly higher values in the Targu Jiu area compared to Rovinari (fig. 1).

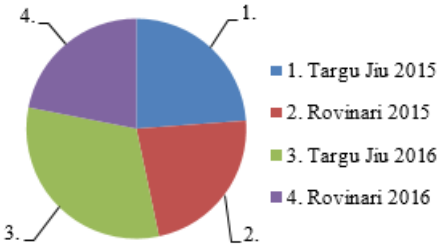

Fig. 1. Distribution of annual mean lead concentrations in Targu-Jiu and Rovinari

If in 2015 the average annual lead concentration calculated for the Targu Jiu area was higher than that at Rovinari by 4%, in 2016 this difference increased to 30%. By reporting the average annual concentrations of the two zones at the limit value, the one calculated for 2016 for the Targu Jiu area was 0.7% and the other 0.5% of the allowed limit.

If reference has been made to the monthly average concentrations of the two areas, it is noted that while for Targu Jiu they showed the highest value in May 2015 and accounted for 29% of the total of the average monthly concentrations, under the conditions of a monthly data capture of 84%, for the Rovinari area, the average monthly concentration with the highest value was also determined in 2015, in February, representing 20% of the total amount, with a monthly catch of 54% (fig. 2)

The monthly average concentrations with the lowest values of the two areas were also recorded in 2015 but at different times. Thus, for the Targu Jiu area, the average monthly concentration with the lowest value was calculated in July and accounted for 4.5% of the total of the average concentrations corresponding to 2015 and for the Rovinari area in June and accounted for 9% total amount.

Following the evolution of the lead concentrations of the two areas under study, it was found that the values representing the highest concentrations measured over 24 h were also recorded in 2015.Thus, for the Targu Jiu area, the highest value was registered in May and accounted for 12% of the total of the daily concentrations corresponding to this period of the year, and for the Rovinari area in January and accounted for 29% of the total of the daily concentrations of this months.The frequency of these concentrations of lead in the air was registered only in one day during May or January.

Regarding the daily lead concentrations with the lowest values for the Targu Jiu area, these were registered in 2015, during several months (May, June, July and August), the frequency of occurrence within one month being between 3.3% and 7.7%. For the Rovinari area, the lead concentration with the lowest value was recorded in 2016, in May and July, with only one occurrence over a month.

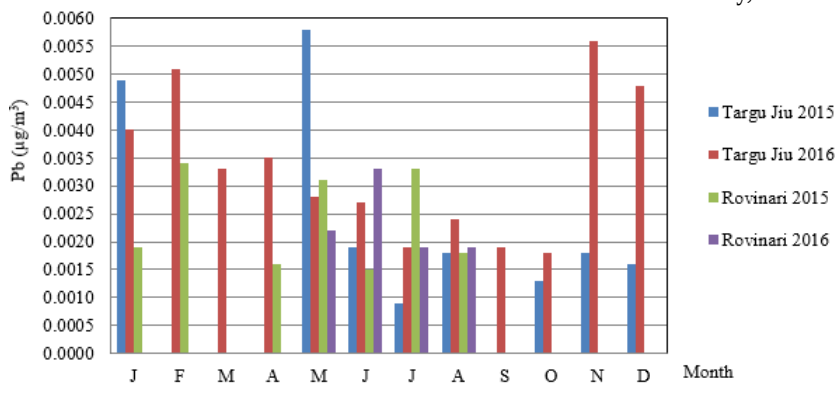

Fig. 2. The variation of the monthly average concentrations of Pb in the areas of Targu Jiu and Rovinari

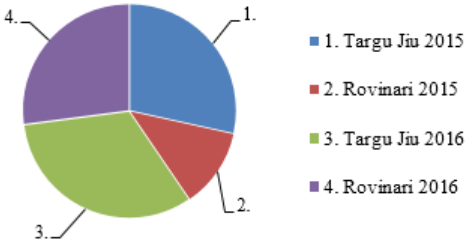

Fig. 3. Distribution of annual mean arsenic concentrations in Targu-Jiu and Rovinari

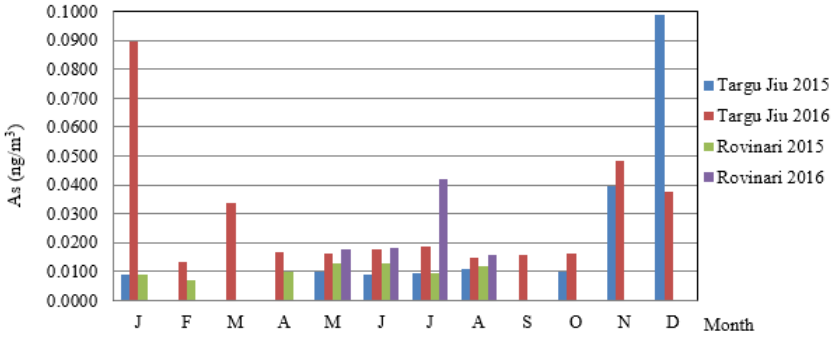

Fig. 4. The variation of the monthly average concentrations of arsenic in the areas of Targu Jiu and Rovinari

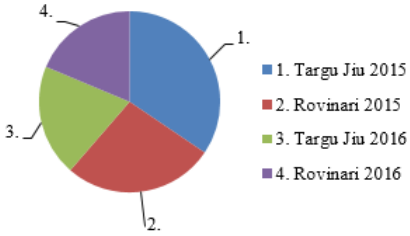

Fig. 5. Distribution of annual mean cadmium concentrations in Targu-Jiu and Rovinari

In the case of arsenic, higher annual mean concentrations were recorded in the Targu Jiu area compared to Rovinari (fig. 3)

The average annual arsenic concentration calculated for the Targu Jiu area was 58% higher than the Rovinari area in 2015 and 17% in 2016. Reporting the average annual concentrations of the two areas at the limit value revealed that in 2015 they accounted for 0.4% for the Targu Jiu area and 0.2% for the Rovinari area and respectively 0.5 and 0.4% in 2016. An analysis of the average monthly arsenic concentrations revealed that, unlike lead, the highest values were recorded for the Targu Jiu area in 2015 and for Rovinari in 2016 (fig. 4).

Thus, for the Targu Jiu area, the highest monthly average concentration was calculated in December 2015, representing about 4% of the sum of the daily concentrations of that period, and was above the highest monthly average concentration for the Rovinari area in 2015 with 87%.

In 2016, the monthly average concentration with the highest value for the Targu Jiu area was recorded in January, representing about 3% of the total of the daily concentrations of this period, and was above the monthly average concentration with the highest value of the Rovinari area that has been registered in July, 53%.

Following the presence of arsenic in the air, it was found that the highest daily concentrations were registered in 2016, both for Targu Jiu and Rovinari. However, it should be noted that the value of the daily concentration in Targu Jiu, recorded in January, was higher than that corresponding to the Rovinari area, registered in July, by 70%.

Regarding the total of the daily arsenic concentrations, the maximum value for the Targu Jiu area represented about 30% of the area, and the one corresponding to the Rovinari area, 17%. Referring to the lowest daily concentration, it was recorded for the Targu Jiu area in 2016, february, and accounted for only 0.2% of the total of the corresponding daily concentrations of this month, being at the same time the most lower value that was measured over the two years of study.

For the Rovinari area, the lowest daily concentration was recorded in 2015, with three months (May, July, August), and ranged from 0.8 to 1% of the total of the daily concentrations.

Regarding cadmium concentrations, we find that higher values were recorded in the Targu Jiu area compared to Rovinari.In 2015, the annual average concentration corresponding to Targu Jiu area was higher than that calculated for the Rovinari area by 22% (fig. 5).

In 2016, the difference between the annual average concentration corresponding to Targu Jiu and Rovinari area was approximately 6%. If we report the average annual concentrations to the limit value for cadmium in the air, they represented 9.7% for Targu Jiu and 7.5% for the Rovinari area in 2015 and 5.6 and 5.2% respectively 2016, from the allowed limit. By comparing the values of the mean monthly concentrations of the two areas over the two years of study, some observations can be made about the presence of cadmium in the air.

Thus, the average monthly concentration with the highest value was calculated for the area of Targu Jiu in 2015, this being above the average monthly concentration with the highest value corresponding to the Rovinari area by 16%, recorded also in the year 2015 (fig. 6).

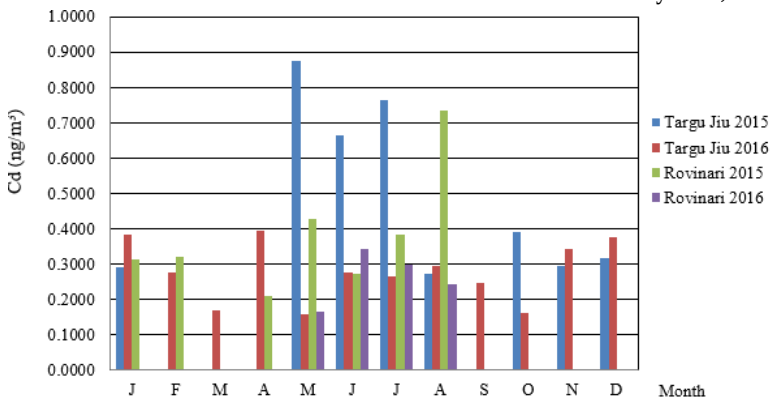

Fig. 6. The variation of the monthly average concentrations of cadmium in the areas of Targu Jiu and Rovinari

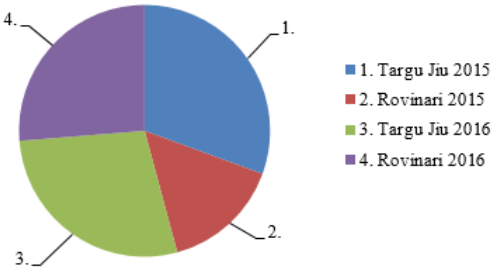

Fig. 7. Distribution of annual mean nickel concentrations Targu-Jiu and Rovinari

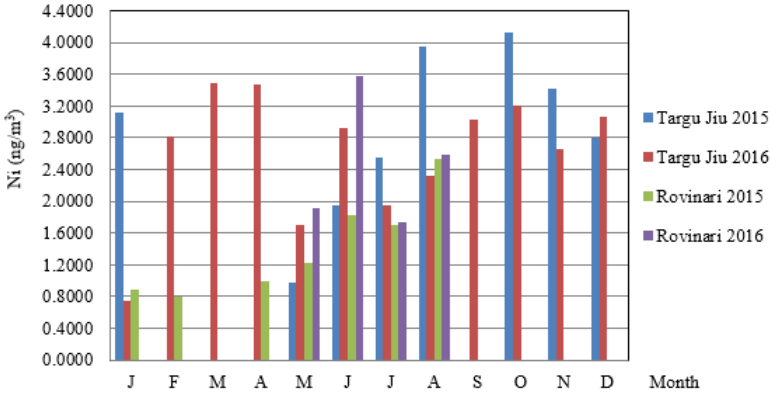

Fig. 8. The variation of the monthly average concentrations of nickel in the areas of Targu Jiu and Rovinari

The same finding is also valid for the year 2016, the monthly average concentration with the highest value also being recorded in the Targu Jiu area, the difference between that and Rovinari area being about 13%.Regarding the monthly average concentration with the lowest value, it was registered at the level of 2016 in the Targu Jiu area and was below the lowest air cadmium concentration level corresponding to the Rovinari area recorded also in 2016 by 4.6 %.

Regarding the daily cadmium concentrations, the highest value (5.1072 ng/m^3) was registered in 2015 in the Targu Jiu area, representing almost a quarter of the total of the daily concentrations and was 42% higher than the highest daily concentration of Rovinari (2.9713 ng/m^3), also registered in 2015, which accounted for 16% of the total of the daily values corresponding to that period.

The daily concentration with the lowest value (0.0017 ng/m^3) was recorded in the Targu Jiu area, this being below the lowest daily concentration measured in the Rovinari area (0.0091 ng/m^3) by 81%, both of 2015.

In case of nickel, taking into account the annual average, monthly and daily average concentrations, in most cases higher concentration values were found for the Targu Jiu area compared to Rovinari.In both 2015 and 2016, the annual average nickel concentrations showed higher values for the Targu Jiu area than Rovinari, without exceeding the limit value (fig. 7).

The average annual concentration with the highest value was recorded in 2015 in the Targu Jiu area and accounted for 14.3% of the limit value, and the highest for the Rovinari area was in 2016 and accounted for 12.3% of the allowed limit. In 2015, the annual average concentration calculated for Targu Jiu was above 50% in Rovinari and by 6% in 2016.For monthly average concentrations the situation is different, both in terms of maximum and minimum values.At 2015 the average monthly concentration with the highest value (4.1160 ng/m^3) was registered in Targu Jiu area and it was above the maximum monthly value corresponding to the Rovinari area (2.5407 ng/m^3) by about 38% (fig. 8).

In 2016, the average monthly nickel concentration with the highest value was recorded in the Rovinari area (3.5766 ng/m^3) with only 2.4%, this being above the concentration with the highest value corresponding to the area of Targu Jiu (3.4914 ng/m^3) with only 2.4%.By comparing the average monthly concentrations with the lowest values of the two areas, the situation is the same.

In 2015 the average monthly nickel concentration with the lowest value (0.9786 ng/m^3) recorded in the Targu Jiu area was above that corresponding to the Rovinari area (0.8024 ng/m^3) by over 18%.

At the level of 2016, the monthly average nickel concentration with the lowest value recorded in the Rovinari area (1.7437 ng/m^3) was 73% above that corresponding to Targu Jiu area (0.7368 ng/m^3). In the case of the daily nickel concentrations representing the highest and lowest values the situation is similar.

At the level of 2015, the highest daily nickel concentration recorded in the Targu Jiu area (12.8943 ng/m^3) was above the highest daily value of Rovinari (11.2827 ng/m^3) with 12.5%, representing 24 and 41% respectively of the total of the corresponding daily concentrations.

In 2016, the daily nickel concentration with the highest value was also recorded in Targu Jiu (9.6439 ng/m^3) and was above that corresponding to the Rovinari area (7.7280 ng/m^3) by about 20%, representing 12 and 7.5% of the total of the daily concentrations corresponding to that period.

Referring to the daily nickel concentrations with the lowest values recorded in the two areas at the level of the two years of study, lower concentrations were measured this time in the Targu Jiu area. Thus, in 2015, the daily nickel concentration of the lowest value was close to half of the minimum daily concentration of the Rovinari area. At 2016, the difference between the lowest nickel concentration value of Rovinari and Targu Jiu was even more pronounced, reaching 78%.

Conclusions

By analysing these data regarding heavy metals content in PM_{10} in Targu-Jiu and Rovinari area for two years of study, the followings conclusion can be drawn:

-for both Targu Jiu and Rovinari the concentrations of heavy metals in the air were below the limit value set for each heavy metals analyzed;

-higher concentrations of lead in the air were recorded in the Targu Jiu area, compared to the Rovinari area. In 2015, the annual average concentration was 4% higher, and in 2016 by 30%.

-for arsenic, higher concentrations were recorded in the Targu Jiu area compared to the Rovinari area, 58% in 2015 and 17% in 2016.

-The same finding is valid for cadmium, higher values being recorded in Targu Jiu area compared to Rovinari, by 22% in 2015 and by 5.6% in 2016.

-Nickel concentrations have evolved in the same direction, being higher in Targu Jiu by 50% compared to Rovinari in 2015 and by 6% in 2016.

-Reporting the annual mean concentrations of the analyzed elements to their limit values allowed, the following descending order of their presence in the air has been determined: Ni> Cd> Pb> As.

-The highest daily nickel concentration measured during the two years of study was recorded for in the Targu Jiu area, January2015, and accounted for 24% of the total of the corresponding daily concentrations of this month.

-The lowest daily lead concentration was registered in the Rovinari area during May and July 2015 and accounted

for about 0.2% of the total of the daily concentrations of these periods.

According to these, it can be say that air in the Targu-Jiu and Rovinari areas is clean regarding the content of heavy metals in particulate matter. This can be due to the measures that had been taken to reduce air pollution from industrial areas.

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