STUDY OF FINE PARTICLES PM10 AND PM2.5 AND THREE ASSOCIATED HEAVY METALS (Pb, Zn AND Cu) IN THE CITY OF TIARET, ALGERIA

Omar SAFI and Mohamed Islam BOUACHA
Laboratory of Agro-Biotechnology and Nutrition in Semi-arid Areas, Faculty of Natural and Life Sciences, Department of Biology, Compuskarman University, Ibn Khaldoun of Tiaret, Algeria.
E-mail: dr.omarsafa@gmail.com, islem2989@gmail.com

Abstract
The purpose of the study is to estimate the mass concentrations of PM10 and PM2.5, collected through the use of a DEKA TI two-stage impactor, and the concentrations of three heavy metals (Pb, Zn, and Cu) associated through flame atomic absorption spectrometry (FAAS), on 92 sites covering all the urban fabric of the city Tiaret. The results obtained revealed mean concentrations of PM10 and PM2.5 of 37.11 ± 5.36 µg/m$^3$ and 20.87 ± 4.36 µg/m$^3$, respectively. The content of ETMs, assayed in this work, records average concentrations of 0.25 ± 0.0756 µg/m$^3$, 0.50 ± 0.0767 µg/m$^3$ and 0.236 ± 0.0498 µg/m$^3$ respectively for lead, copper and zinc adsorbed at the PM10 fraction. However, these ETMs (Pb, Cu, Zn) adsorbed to the PM2.5 fraction show mean concentrations of 0.23 ± 0.0803 µg/m$^3$, 0.28 ± 0.0902 µg/m$^3$ and 0.186 ± 0.0307 µg/m$^3$, respectively.

Key words: PM10, PM2.5, Pb, Zn, Cu, DEKA TI impactor, Tiaret city.

Introduction
In addition to gases, the atmosphere contains suspended solids in the liquid and solid phase (aerosols), representing a complex mixture of chemical substances, organic and inorganic, which are grouped under the general term “suspended particles”. These particles in suspension are often designated by the abbreviation PM which comes from “Particulate Matter”, of very varied origin, come from natural sources and / or anthropic and are emitted through various physicochemical processes which influence their size distribution, their concentration and their chemical composition. Among these particulate matters we distinguish:

PM10 and PM2.5 which have an aerodynamic diameter of less than 10 µm and 2.5 µm respectively (Donaldson and Stone, 2003; Goulauvie, 2009; Thorpe and Harrison, 2008).

Particle pollution in the city of Tiaret is underestimated because of the scarcity of work done and the absence of air quality measurement stations. With the exception of some local work on bio-monitoring of air quality (Omar et al., 2015; Maatoug et al., 2012; Maatoug et al., 2010), no studies were recorded on fine particles (Aerosols).

The purpose of the research work undertaken in this study is to estimate the mass concentration of PM10 and PM2.5 atmospheric particles collected and heavy metals (Pb, Cu, Zn) adsorbed at each fraction in the city of Tiaret, in order to develop air pollution maps by MPs. To do this, we performed atmospheric urban particulate sampling by impaction using a two-stage DEKA TI cascade impactor and an absorption rate of 30 L/min at 92 sites.

Material and Methods
Presentation of the study area
The study area represents an urban metropolis with significant evolutionary kinetics, located in the central-western part of Algeria, the city of TIARET represents a city environment with a strong demographic growth.

The region of Tiaret is located in semi-arid bioclimatic stage with cool winter. Average temperatures are around 15.7°C with a minimum of 8.7°C and a maximum of
23.2°C during 2016 (webmaster 1). The average rainfall is 334.04 mm.

Given the absence of a large industrial park, the main source of pollutant emissions is the car fleet. This consists of 151,757 vehicles, all types combined, of which 40% are gasoline and 56% are diesel, while LPG vehicles represent only 4%. Indeed, this park is heterogeneous due to the variety of vehicles that constitute it (private or utility vehicle, gasoline or diesel, recent or old, etc.). (Transport Directorate of Tiaret, 2016).

The city of Tiaret is served by three main road axes namely RN 14, RN 90 and RN 23, and two wilaya roads that are CW 07 and CW 11 (fig. 1).

The methodology adopted is based around sampling at various points distributed so as to cover the whole city. Particulate sampling involves collecting large masses of PMs for each site. The filter used to capture the PMs is recovered at the end of the sampling, and is not left for prolonged periods, so as not to undergo mass variations due to particle loss, passive deposition or volatilization. Note that particle collection filters are weighed before and after sampling by using a scale with an accuracy of 1µg. This is indeed to determine the mass concentrations of the particles, expressed in µg / m³, by deviating the mass of the sample collected on the volume of air absorbed. The concentrations obtained allow the development of the air pollution maps of the study area by PM10 and PM2.5 fine particles.

Sampling adopted in this study is to take samples at the points of high concentration of traffic all times additional samples are made equal distance to cover all the urban fabric (fig. 2). This is to have as much information as you want. However, the levy was not without difficulty. Indeed, in case of humidity or high wind speed, a systematic stop sampling is observed. Sampling is carried out during the summer period from May to the end of August of 2016 on 92 sites.
The collected samples are subjected to a laboratory analysis, which are put in an acid medium and then diluted, in order to analyze them through the atomic absorption spectrometry for the estimation of the concentrations of the heavy metals associated with the PMs according to the large lines of standards EN 14902. The adopted method recommends a dissolution of the elements targeted by an acid attack in a mineralizer (closed environment). To avoid contamination of the samples, pure reagents are recommended. The recommended acid mixture is to use 4 volumes of nitric acid (HNO₃) for one volume of oxygenated water (H₂O₂). The reactors are placed in the microwave oven for a 45 min mineralization at a maximum temperature of 200°C. After cooling (1 to 2 h), the mineralizes are transferred to polycarbonate tubes previously washed with acid (HNO₃) and adjusted to 50 ml with ultra pure water. The analyzes are carried out by flame atomic absorption spectrophotometry (FAAS) according to the instructions recommended by the manufacturer.

### Results and Discussion

The objective of this study is to estimate the concentrations of PM10, PM2.5 and associated heavy metals (Pb, Zn and Cu).

#### Concentrations of PMs and associated heavy metals

Table 1 shows the descriptive statistics of the concentrations of PMs and adsorbed metal trace elements recorded in the study area. The results obtained are expressed in μg/m³.

Table 1: Concentrations of PMs and Associated Heavy Metals (μg/m³).

<table>
<thead>
<tr>
<th></th>
<th>Min</th>
<th>Max</th>
<th>Mean</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM10</td>
<td>18.00</td>
<td>63.00</td>
<td>37.11</td>
<td>5.3598</td>
</tr>
<tr>
<td>Pb</td>
<td>0.05</td>
<td>0.50</td>
<td>0.25</td>
<td>0.0756</td>
</tr>
<tr>
<td>Cu</td>
<td>0.31</td>
<td>0.66</td>
<td>0.50</td>
<td>0.0767</td>
</tr>
<tr>
<td>Zn</td>
<td>0.01</td>
<td>0.41</td>
<td>0.236</td>
<td>0.0498</td>
</tr>
<tr>
<td>PM2.5</td>
<td>11.12</td>
<td>34.00</td>
<td>20.87</td>
<td>4.3604</td>
</tr>
<tr>
<td>Pb_{PM2.5}</td>
<td>0.15</td>
<td>0.60</td>
<td>0.23</td>
<td>0.0803</td>
</tr>
<tr>
<td>Cu_{PM2.5}</td>
<td>0.10</td>
<td>0.90</td>
<td>0.28</td>
<td>0.0902</td>
</tr>
<tr>
<td>Zn_{PM2.5}</td>
<td>0.12</td>
<td>0.32</td>
<td>0.186</td>
<td>0.0307</td>
</tr>
</tbody>
</table>

The collected samples are subjected to a laboratory analysis, which are put in an acid medium and then diluted, in order to analyze them through the atomic absorption spectrometry for the estimation of the concentrations of the heavy metals associated with the PMs according to the large lines of standards EN 14902. The adopted method recommends a dissolution of the elements targeted by an acid attack in a mineralizer (closed environment). To avoid contamination of the samples, pure reagents are recommended. The recommended acid mixture is to use 4 volumes of nitric acid (HNO₃) for one volume of oxygenated water (H₂O₂). The reactors are placed in the microwave oven for a 45 min mineralization at a maximum temperature of 200°C. After cooling (1 to 2 h), the mineralizes are transferred to polycarbonate tubes previously washed with acid (HNO₃) and adjusted to 50 ml with ultra pure water. The analyzes are carried out by flame atomic absorption spectrophotometry (FAAS) according to the instructions recommended by the manufacturer.

The collected samples are subjected to a laboratory analysis, which are put in an acid medium and then diluted, in order to analyze them through the atomic absorption spectrometry for the estimation of the concentrations of the heavy metals associated with the PMs according to the large lines of standards EN 14902. The adopted method recommends a dissolution of the elements targeted by an acid attack in a mineralizer (closed environment). To avoid contamination of the samples, pure reagents are recommended. The recommended acid mixture is to use 4 volumes of nitric acid (HNO₃) for one volume of oxygenated water (H₂O₂). The reactors are placed in the microwave oven for a 45 min mineralization at a maximum temperature of 200°C. After cooling (1 to 2 h), the mineralizes are transferred to polycarbonate tubes previously washed with acid (HNO₃) and adjusted to 50 ml with ultra pure water. The analyzes are carried out by flame atomic absorption spectrophotometry (FAAS) according to the instructions recommended by the manufacturer.

The collected samples are subjected to a laboratory analysis, which are put in an acid medium and then diluted, in order to analyze them through the atomic absorption spectrometry for the estimation of the concentrations of the heavy metals associated with the PMs according to the large lines of standards EN 14902. The adopted method recommends a dissolution of the elements targeted by an acid attack in a mineralizer (closed environment). To avoid contamination of the samples, pure reagents are recommended. The recommended acid mixture is to use 4 volumes of nitric acid (HNO₃) for one volume of oxygenated water (H₂O₂). The reactors are placed in the microwave oven for a 45 min mineralization at a maximum temperature of 200°C. After cooling (1 to 2 h), the mineralizes are transferred to polycarbonate tubes previously washed with acid (HNO₃) and adjusted to 50 ml with ultra pure water. The analyzes are carried out by flame atomic absorption spectrophotometry (FAAS) according to the instructions recommended by the manufacturer.
PM2.5, respectively, with a peak of 0.9 μg/m³ for copper associated with PM2.5. Zinc concentrations are oscillated between a minimum of 0.01 μg/m³ and 0.12 μg/m³ and a maximum of 0.41 μg/m³ and 0.32 μg/m³, with an average of 0.24 ± 0.05 μg/m³ and 0.19 ± 0.03 μg/m³ respectively for PM10 and PM2.5.

A better appreciation of the spatial behavior of the fine particles is allowed through the realization of a pollution map. Figure 03 shows pollution maps of the study area by PM10 and PM2.5.

For PM10, the classes obtained are classified according to the standards proposed by WHO (2005) and the decree of the European Union (2008). Class 1 represents concentrations that do not exceed the guideline of 20 μg/m³ (WHO, 2005), the second class with concentration values lower than the air quality objective of 30μg/m³ (intermediate targets 3 according to WHO). The third class occupies the largest part of the study area with concentrations above 30 μg/m³, but does not exceed the limited value of 40 μg/m³ (J-O, EU, 2008). The fourth class with concentrations between 40 and 50μg / m3, also occupies a significant part of the study area, located mainly in the north-west and south parts of the city. Finally, the last class represents the areas with concentrations that exceed the intermediate target 2 (50 μg/m³) and lower than the intermediate target 1 (70 μg/m³), which has been found in a few areas, namely:

- the intersection of the national road 23, national road 14 and the state road 7;
- the south of the national road 90.

For PM2.5, the concentrations obtained exceed the annual averages proposed by the WHO in 2005, which is 10 μg/m³. Most of the city of Tiaret has a lower PM2.5 concentration than the intermediate target 2 of 25 μg/m³ (WHO, 2005), while in the center and south of the study area. Note a class represents concentrations that exceed the intermediate target 2 and lower than the intermediate target 1 (35 μg/m³).

According to Popescu (2011), 80% of urban PM emissions are caused by road traffic, and this traffic is the main source of heavy metal emissions. It is also that the concentration of atmospheric pollutants would be maximum in the territory bordering the major axes of circulation. This means that road traffic is a major cause of pollution (Stella, 2016; CARRIER, 2015; Krzyzanowski et al., 2005; Reponen et al., 2003; Kukkonen et al., 2003).

In their study on fine particles from road traffic in Africa, Naidja et al. (2017) mentioned that in the cities of Constantine and Algiers the PM10 comes mainly from road traffic with average concentrations of 80 μg/m³ and 34.8 μg/m³, respectively.

However, the metallic elements come from various sources, but the main non-industry source is road traffic (Mbengue, 2013; Popescu, 2011; Hugolin et al., 2005; Morawska & Zhang, 2002). In addition, Ntziachristos et al. (2007) also reported that car emissions contribute to the enrichment of several metal elements, namely Pb, Ba, Ca, Cu, Sb and Zn. Thus, according to Stella (2016), lead (Pb) is among the main metals emitted by road traffic with a percentage of 45%.

**Conclusion**

The results obtained during this experiment show that the study area has significant PM concentrations, and exceed in several sites the values recommended by the World Health Organization (2005). The PM10 fraction shows significant concentrations with a maximum of 63 μg/m³ and an average of 37.11 ± 5.3598 μg/m³, exceeding in several sites the values recommended by the World Health Organization (2005), even of the European Union (2008) as a limited value. PM2.5 concentrations record a maximum of 34 μg/m³ and an average of 20.87 ± 4.3604 μg/m³.

Nevertheless, lead, a very toxic metal element, is responsible for several diseases. The particles collected showed significant proportions of this metal associated with them. Knowing that lead comes from several anthropogenic sources including road traffic, especially diesel engines, which is one of the main emitters. Lead concentrations were between 0.05 μg/m³ and 0.50 μg/m³ for PM10 and between 0.15 μg/m³ and 0.60 μg/m³ for PM2.5. These values are stressful since they are greater than or equal to the limited value proposed by the European Union (0.5 μg/m³) in several sites. Knowing that lead comes from several anthropogenic sources whose road traffic and especially diesel engines, is one of the main emitters.

Other trace elements (zinc and copper) adsorbed to PM10 particles were assayed in this study; their concentrations are respectively represented by the following averages: 0.236 ± 0.498 μg/m³ and 0.50 ± 0.0767 μg/m³, respectively. Although the average concentrations of these two elements adsorbed to the PM2.5 fraction are of the order of 0.28 ± 0.0902 μg/m³ for copper and 0.186 ± 0.0307 μg/m³ for zinc.

**Acknowledgements**

We present our sincere thanks to all who participated in the realization of this modest work.
References


