



## Evaluation of airborne particulate matter pollution in Kenitra City, Morocco

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### ABSTRACT

Two size fractions of atmospheric particulate matter < 2.5 µm and 2.5-10 µm were collected in Kenitra City from February 2007 to February 2008. The sampling was done using a Gent Stacked sampler on nuclepore polycarbonate filters and the collected filters were analyzed using Total Reflection X-Ray Fluorescence (TXRF) and Atomic Absorption Spectroscopy (AAS). The particulate matter trends show higher concentrations during the summer as compared to other seasons. The highest concentrations were obtained for Ca in coarse particles and Fe for fine particles. However, the lowest concentrations were observed for Cd in both particulate sizes. The principal component analysis (PCA) based on multivariate study enabled the identification of soil, road dust and traffic emissions as common sources for coarse and fine particles.

**Keywords:** X-ray fluorescence, cluster analysis, principal component analysis.

## Avaliação da poluição de material particulado de aviação em Kenitra, Marrocos

### RESUMO

Duas frações de tamanhos <2,5 µm e 2,5-10 µm de material particulado atmosférico foram coletadas na cidade de Kenitra de fevereiro de 2007 a fevereiro de 2008. A amostragem foi feita utilizando-se um amostrador de Gent empilhados em filtros de polycarbonato Nuclepore e os filtros foram analisados para os elementos de reflexão total usando fluorescência de raios X (TXRF) e Espectroscopia de Absorção Atômica (AAS). As partículas tiveram tendência de apresentar maior concentração durante a temporada de verão em comparação com outras estações. As maiores concentrações de partículas grossas foram de Ca e de partículas finas de Fe. No entanto, as concentrações mais baixas foram observadas para o Cd em ambas as frações de tamanho. A análise de componentes principais (ACP) com base na análise multivariada permitiu a identificação de emissões do solo, de poeira de estrada, e do tráfego como fontes comuns de partículas grossas e finas.

**Palavras-chave:** Fluorescência de raios X, análise de agrupamento, componentes principais.

## 1. INTRODUCTION

Air pollution has become a matter of global concern because of its impact on human health and environmental quality. The awareness of air pollution has led to numerous studies on the chemical composition of ambient aerosols and the determination of pollution sources. Atmospheric aerosols influence many atmospheric processes and have adverse human health effects, affecting both the respiratory and cardiovascular systems (Laden et al., 2000; Michael and Daniel, 2005; Ruzer and Harley, 2004; Li et al., 2009).

A major component in air urban pollution is particulate matter (PM) which can be coarse or fine. Coarse particles can be regarded as those with a diameter ranging from 2.5 to 10  $\mu\text{m}$  (PM<sub>2.5-10</sub>); and fine particles less than 2.5  $\mu\text{m}$  (PM<sub>2.5</sub>). Coarse particles usually contain materials from the earth's crust and dust from vehicles and industrial plants; while fine particles contain the secondary formed aerosols, combustion particles and re-condensed organic and metallic vapours (Jacobson, 2002).

The chemical characterization of particulate matter could be elaborated using many multi-elemental techniques. Non-destructive nuclear and related analytical techniques such as X ray fluorescence analysis (XRF) have already proven to be well suited for the routine analysis of aerosols samples (Chueinta et al., 2000; Biswas et al., 2003; Cohen et al., 2004; Kim Oanh et al., 2006; Santoso et al., 2008). It provides multi-element capability needed in creating databases to be used for assessing air pollution, source apportionment or time-trend assessments. This ability to quickly and efficiency produce large data sets for statistically characterizing and fingerprints pollution sources as well as estimating different source contributions is critical to the understanding of air pollution.

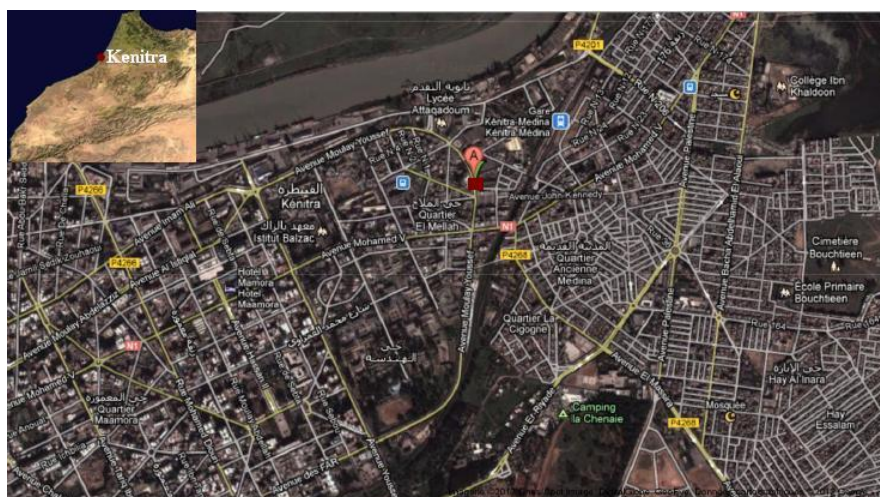
In Morocco, air pollution is not well estimated. The existing studies have a local character. These studies were initiated in the beginning of the 90s by the Department of Environment in the cities which suffer significantly from atmospheric pollution (Morocco, 2000; 2001; 2002; 2003). Therefore, the present paper will present the main results of the analyses of particulate matter (coarse and fine particles) samples in Kenitra city. An evaluation of the probable sources of emission in the studied area will also be presented.

## 2. MATERIAL AND METHODS

### 2.1. Sampling

The Gent stacked filter unit sampler (Hopke et al., 1997) has been used for the collection of fine (< 2.5  $\mu\text{m}$ ) and coarse (2.5 - 10  $\mu\text{m}$ ) particles on Nuclepore polycarbonate filters of 8  $\mu\text{m}$  and 0.4  $\mu\text{m}$  pore size, respectively. Samples were collected at an average flow rate of 16 lpm for a sampling period of 24 hours. The sampler was placed near a bus station (Figure 1) located in the center of Kenitra city. There is a very high volume of motor traffic at this site, and it includes a parking for buses and many "big taxis". It is also bordered by railway. The samplers were installed in a courtyard, separated from vehicles by a wall about 3 m high.

Kenitra city is located about 50 km from Rabat (the kingdom of Morocco) and borders the Atlantic Ocean. Wind direction is predominantly West to Northwest (coming from the sea). In addition to being an important transportation hub, the city's industry is based upon the activities of its port and small businesses. The samplings were performed one day per week, from May 2007 to May 2008. A total of 126 samples (63 for fine and 63 for coarse) were taken during this period.



**Figure 1.** Location of the sampling site (noted as ‘A’ in the map) in Kenitra City.

## 2.2. Sample Preparation and Analysis

Multi-elemental analysis of filter samples was performed by Total X-Ray Fluorescence (TXRF). This technique needs to bring into solution the samples to be analyzed. Accordingly, the loaded filters were decomposed with 10 ml on concentrated  $\text{HNO}_3$  in a microwave oven during time 30 min. After decomposition and complete cooling of the solutions, 50  $\mu\text{g}$  of Selenium were added to each sample as internal standard, and aliquots of 25  $\mu\text{l}$  were placed onto quartz carriers for TXRF measurements.

The TXRF system employed is that installed in the National Centre of Energy, Sciences and Nuclear Techniques (CNESTEN) in Morocco. This module is equipped with a 2 kW-power fine-focus X-ray tube with a molybdenum anode usually operating at 30 mA and 50 kV. The X-ray beam is monochromatized by use of a multilayer (W/C) crystal. The fluorescent X-rays of the sample are detected by a Si(Li) detector with a resolution of 165 eV at 5.9 keV and then analyzed by a Canberra S100 multi-channel analyzer card coupled to a computer for data storage and analysis. To complete this study, we used the Atomic Absorption Spectroscopy (AAS), available in the European Centre for Research and Teaching Environmental Geosciences (CEREGE) in Aix en Provenance in France, to evaluate the contents of Al and Na.

## 2.3. Statistical Analysis

Over the last two decades, multivariate analysis has been widely used to identify sources of ambient particles. In this study, Principal Component Analysis (PCA) was used to estimate and identify the possible sources of coarse and fine particles. The main objective of PCA is to reduce a large number of variables to a smaller set of factors that retain most of the information in the original data set (Hopke, 1985; Marcuzzan et al., 2003). In PCA, a set of multiple correlated variables is replaced by a small number of independent variables by orthogonal transformations (Salvador et al., 2003). This transformation is achieved by diagonalizing the correlation matrix of the variables through the computation of eigenvalues and eigenvectors. Each factor explains the maximum total variance of the data set and this set is completely uncorrelated with the rest of the data. The factor concentrations obtained after the Varimax rotation gives the correlation between the variables and the factor. Thus, the chemical elements with higher concentrations in each factor are interpreted as fingerprints of emission source that it represents. In the present study, SPSS software was used to perform multivariate factor analysis.

### 3. RESULTS AND DISCUSSION

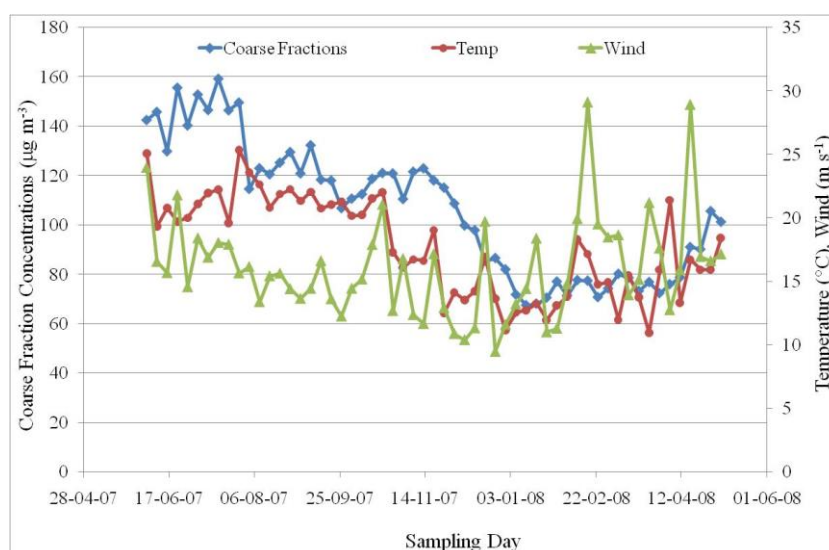
#### 3.1. Concentration Level of Particulate Matter

The summary of the coarse and fine particulate matter collected at the sampling site during the studied period is presented in Table 1. The average mass concentration of coarse and fine particulates were  $110.42 \mu\text{g m}^{-3}$  and  $50.73 \mu\text{g m}^{-3}$  and the highest concentration was equal to  $196 \mu\text{g m}^{-3}$  and  $86 \mu\text{g m}^{-3}$ , respectively. The time series plots of the particulates in both size particles are presented in Figures 2 and 3.

**Table 1.** Statistical summary of the coarse and fine particulate matter mass concentration at Kenitra city during the studied period.

| Parameter     | PM <sub>2.5-10</sub> ( $\mu\text{g m}^{-3}$ ) | PM <sub>2.5</sub> ( $\mu\text{g m}^{-3}$ ) |
|---------------|---|--|
| Mean          | 110.42  | 50.73                                      |
| Median        | 115.12  | 51.32                                      |
| S.D.          | 37.61   | 12.33                                      |
| Maximum       | 195.79  | 85.68                                      |
| Minimum       | 33.18   | 30.35                                      |
| N° of samples | 63  | 63   |

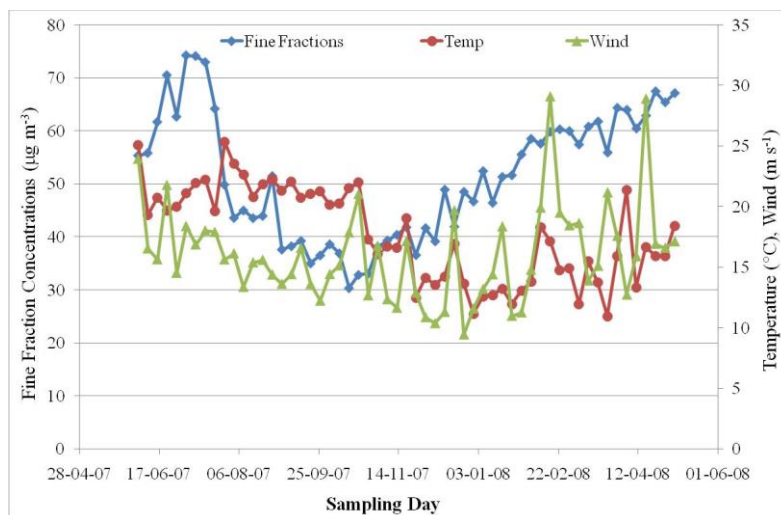
The time series plot indicates that the monthly concentrations of PM<sub>2.5-10</sub> during the winter samplings decrease significantly by half from December to January ( $< 67 \mu\text{g m}^{-3}$ ), followed by a large increase at the beginning of the dry season (from 04/06/07 to 04/11/07) with concentrations ranging between  $106.8$  and  $159.24 \mu\text{g m}^{-3}$ . This seasonal trend could be attributed, in part, to the meteorological conditions. In fact, it was found that the higher values of PM<sub>2.5-10</sub> correspond to higher temperatures and lower wind speed values and vice versa (Figure 2).



**Figure 2.** Variations of concentrations of coarse particulates in function of metrological parameters (wind and temperature) at Kenitra site.

However, from the beginning of the winter samplings until January, the fine particles (PM<sub>2.5</sub>) showed an inverted behaviour to that observed for coarse particles. After this period,

the fine particles show a relatively stable profile with two significant peaks: the first from 10/06/2007 to 22/07/2007 and the second from 30/03/2008 to 11/05/2008 with concentrations of (55.83 - 64.18  $\mu\text{g m}^{-3}$ ) and (64.34 - 70.47  $\mu\text{g m}^{-3}$ ), respectively. Nevertheless, no significant correlation was found between the concentrations of PM<sub>2.5</sub> and the meteorological conditions as it can be observed in Figure 3.



**Figure 3.** Variations of concentrations of fine particulates in function of meteorological parameters (wind and temperature) at Kenitra site.

### 3.2. Metal concentrations in particulate matter

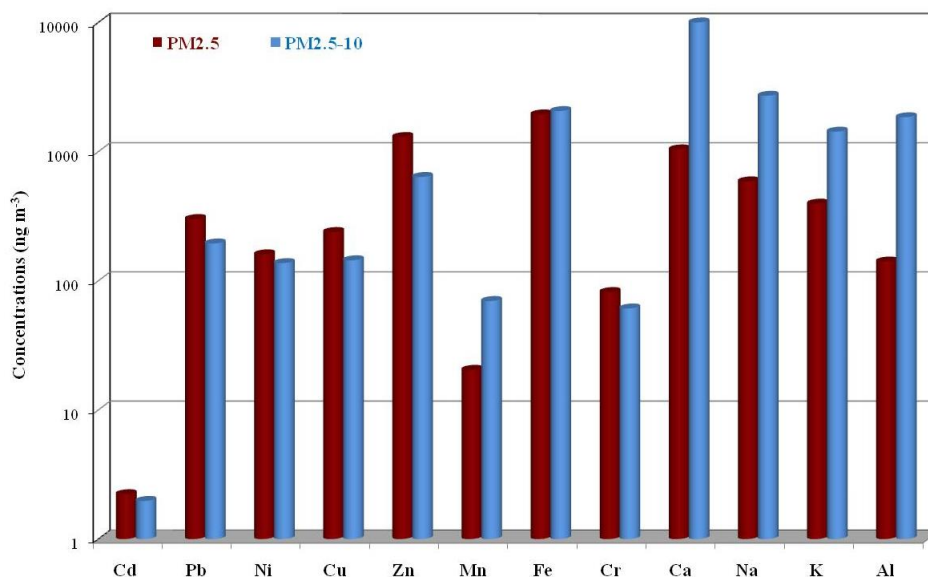
The results of elemental concentrations obtained for PM<sub>2.5</sub> and PM<sub>2.5-10</sub> and their standard deviations are presented in Table 2. The mean values presented in Table 2 are obtained from a data set of 63 samples. Twelve elements were determined for all the samples in coarse and fine particles; average concentrations of various elements range from few  $\text{ng m}^{-3}$  (ex. Cd) to thousands of  $\text{ng/m}^3$  (ex. Ca and Fe).

**Table 2.** The mean and standard deviations of elemental concentrations of coarse and fine particulate matter at Kenitra site.

| Parameter | PM <sub>2.5-10</sub> ( $\text{ng m}^{-3}$ ) |         | PM <sub>2.5</sub> ( $\text{ng m}^{-3}$ ) |        |
|-----------|---|---------|--|--------|
|           | Mean  | S.D.    | Mean                                     | S.D.   |
| Al        | 1848.34                                     | 267.48  | 140.07                                   | 51.19  |
| Ca        | 11300.40                                    | 2016.81 | 1040.32                                  | 169.18 |
| Cd        | 1.98  | 0.25    | 2.23                                     | 0.29   |
| Cr        | 60.53                                       | 9.75    | 81.38                                    | 10.47  |
| Cu        | 144.30                                      | 27.08   | 239.53                                   | 24.77  |
| Fe        | 2051.10                                     | 183.07  | 1938.56                                  | 227.20 |
| K         | 1431.52                                     | 250.35  | 397.20                                   | 43.43  |
| Mn        | 70.16                                       | 6.95    | 20.54                                    | 3.44   |
| Na        | 2706.72                                     | 225.02  | 587.91                                   | 70.18  |
| Ni        | 137.42                                      | 19.69   | 160.57                                   | 43.51  |
| Pb        | 196.04                                      | 29.27   | 303.22                                   | 64.85  |
| Zn        | 634.01                                      | 68.43   | 1301.17                                  | 176.46 |

\* S.D. is Standard Deviation.

Figure 4 shows a comparison of elemental concentrations in fine and coarse particles at Kenitra site. From this diagram, we can observe that, for both fine and coarse particles, Cd is the element with the lowest concentration; however, the highest concentration was recorded for Fe in fine particles and Ca in coarse particles. A comparison of the metal concentrations in both particles indicates that the elements of crustal origin (Ca, Na, K, Al and Mn) are more prevalent in coarse than fine particulates. However, the elements from anthropogenic sources (Cd, Ni, Pb, Cu, Zn and Cr) are more prevalent in fine particulates.

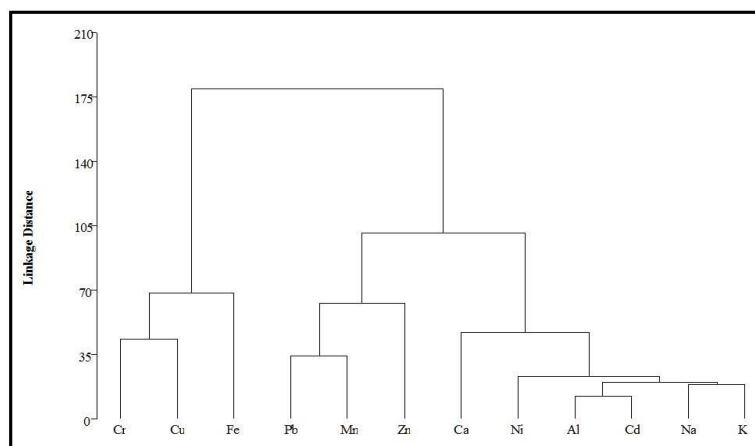


**Figure 4.** Comparison of metal contents in fine and coarse particles at Kenitra site.

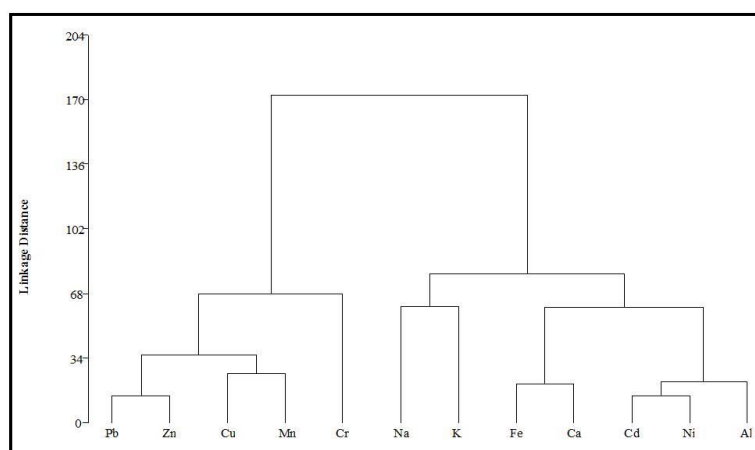
### 3.3. Multivariate analysis

In order to get some insight about the sources of metals and the main correlations among them, Cluster Analysis (CA) and Principal Component Analysis (PCA) were applied.

The correlation matrix [63×12] gives four clusters and four significant PCs which explain 76.37% of fine particles and 80.46% of coarse particles. The obtained dendrograms are presented in Figures 5 and 6 for coarse and fine particles.



**Figure 5.** Dendrogram of CA of metal concentrations in coarse fraction at the studied site.



**Figure 6.** Dendrogram of CA of metal concentrations in fine fraction at the studied site.

The PCA results obtained by Varimax rotated factor analysis for coarse and fine particles are presented in Tables 3 and 4, respectively.

**Table 3.** Varimax rotated PCA factor loadings for coarse particles.

| Elements | Factor 1     | Factor 2     | Factor 3    | Factor 4    |
|----------|--------------|--------------|-------------|-------------|
| Al       | <b>0.84</b>  | 0.10         | 0.05        | -0.11       |
| Ca       | 0.50         | -0.16        | <b>0.66</b> | -0.40       |
| Cr       | <b>-0.64</b> | -0.60        | 0.01        | 0.14        |
| Cu       | -0.58        | 0.12         | <b>0.73</b> | 0.17        |
| Fe       | 0.30         | <b>-0.80</b> | 0.11        | -0.02       |
| Pb       | 0.37         | <b>0.63</b>  | 0.48        | -0.12       |
| Mn       | 0.22         | <b>0.74</b>  | 0.08        | 0.32        |
| Ni       | <b>0.82</b>  | 0.27         | -0.02       | -0.02       |
| Na       | <b>0.86</b>  | -0.19        | 0.22        | 0.13        |
| Cd       | <b>0.93</b>  | 0.05         | -0.13       | -0.02       |
| Zn       | 0.05         | 0.09         | -0.05       | <b>0.94</b> |
| K        | <b>0.86</b>  | 0.06         | 0.10        | 0.12        |

Factor 1 of PCA results of PM<sub>2.5-10</sub> (Table 3) show higher concentrations for Al, Cr, Ni, Na, Cd and K with the maximum percentage of variance (41.84%). This factor represents a mixture of natural soil dust (Al, Na and K) and anthropogenic dust (Cr, Ni, Cd). Therefore, Factor 1 could be assigned to the re-suspension of soil dust contaminated by traffic road. Factor 2 explains 17.48% of the total variance and shows high loadings for Fe (-0.79), Mn (0.74) and Pb (0.63), indicating emissions of road soil dust. The third factor accounts for 10.7% of the total variance. The dominant elements of this factor are Ca and Cu with a PC concentrations of 0.66 and 0.73, respectively, representing soil dust origins. The last factor explains 10.44% of the total variance. The only dominant element for this factor is Zn with a PC concentrations of 0.94 which indicates traffic emission such as breakdown abrasion.

**Table 4.** Varimax rotated PCA factor loadings for fine particles.

| Elements | Factor 1    | Factor 2    | Factor 3     | Factor 4    |
|----------|-------------|-------------|--------------|-------------|
| Cd       | 0.03        | <b>0.76</b> | 0.53         | 0.05        |
| Pb       | <b>0.86</b> | 0.03        | 0.21         | -0.33       |
| Ni       | 0.32        | <b>0.67</b> | 0.50         | -0.20       |
| Cu       | <b>0.85</b> | -0.07       | -0.08        | 0.25        |
| Zn       | <b>0.88</b> | 0.13        | 0.12         | -0.08       |
| Mn       | <b>0.72</b> | 0.12        | -0.36        | 0.06        |
| Fe       | 0.17        | <b>0.85</b> | -0.16        | 0.04        |
| Cr       | 0.22        | -0.09       | <b>-0.77</b> | 0.05        |
| Ca       | 0.06        | <b>0.77</b> | -0.13        | 0.43        |
| Na       | -0.04       | 0.05        | 0.18         | <b>0.90</b> |
| K        | 0.15        | 0.04        | <b>0.62</b>  | 0.16        |
| Al       | -0.28       | <b>0.73</b> | 0.35         | -0.22       |

PCA of fine particulate matter identified four factors with the total variance of 76.37. Factor 1 has high concentrations of Pb (0.86), Cu (0.85), Zn (0.88) and Mn (0.72) which explains 25.40% of the total variance. This factor is associated with elements from traffic emission sources (Veron et al., 1992; Manoli et al., 2002; Samara and Voutsas, 2005; Chang et al., 2009). Thus, factor 1 could be identified as traffic emissions. Factor 2 accounts for 24.41% of the total variance. This factor is a mixture of soil dust (Fe, Ca and Al) and traffic emissions or road dust (Cd and Ni). Therefore, factor 2 could be interpreted as soil/road dust. Factor 3, with 15.79% of the total variance, includes high concentrations for K (0.62) and Cr (-0.77) indicating soil dust origin (Lee and Thi Hieu, 2011). Factor 4 accounts for 10.77% of the total variance. The only dominant element for this factor is Na with a high concentration of 0.79 which clearly indicates its origin from sea salt.

## 4. CONCLUSIONS

Airborne particulate matter in two size particles PM<sub>2.5-10</sub> and PM<sub>2.5</sub> collected at Kenitra City (Morocco) have been analyzed for chemical composition using TXRF and AAS. Time series analysis of particulate matter revealed a seasonal trend with high concentrations during summer period. The contents of chemical elements indicated that Cd is the element that showed the lowest concentrations for both particles. However, Ca presented the highest concentrations in coarse particles and Fe the highest values in the fine particles. Using the principal component, four factors were obtained for both particles. The identified sources for fine and coarse particulates were approximately similar and were mainly related to soil dust and traffic emissions.



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