

Chemical characterization and origin of suspended atmospheric particles in Meknes city in Morocco

H. Ait Bouh^{a,*}, M. Bounakhla^a, F. Benyaich^b, Y. Noack^c, M. Tahri^a, F. Zahry^a.

^a National Center for Energy, Sciences and Nuclear Techniques (CNESTEN), Geochemistry and Chemical Pollution Unit (UGPC) - Earth and Environment Sciences Division (DSTE) B.P.1382 R.P.10001, Rabat, Morocco;

^b Department of Physics, Faculty of Science, Moulay Ismail University, Meknes, Morocco;

^c European Centre for Research and Teaching of Environmental Sciences (CEREGE), Aix en Provence, France.

Abstract

This work is a study of elemental composition of particulate matter (PM-10, with aerodynamic diameter lower or equalizes to 10 μm , collected in Meknes city in Morocco. The campaigns of measure carried out on a traffic site from March 2007 to April 2008. The chemical concentrations of 9 elements (Ca, Cr, Cu, Fe, K, Mn, Ni, Pb and Zn) were determined by Total reflection X-Ray Fluorescence (TXRF), Al was determined by the Atomic Absorption Spectrometry (AAS), whereas the Pb isotopic compositions were determined by Thermo Ionisation Mass Spectrometry (TIMS).

The obtained results show quite significant seasonal variation of the chemical composition for fine and coarse fractions. It should be noted that Pb and Ni concentrations exceeded the air quality standards. The calculation of the Enrichment Factor (EE) revealed that Cr and Pb were attributed mainly to anthropogenic sources. The use of the isotopic extraction of lead confirms the anthropic origin of Pb.

* Corresponding author:
haitbouh@gmail.com

Received 04 April 2016,

Revised 30 Sept 2016,

Accepted 11 Jan 2017

Keywords: Particulate matter, Chemical compositions, Enrichment Factors, isotopic extraction of lead, Meknes.

1. Introduction

The atmosphere is the gaseous envelope surrounding the solid Earth. It consists of a gaseous fluid called air. This one is essential for life because it participates in the process of respiration and photosynthesis of plants. The atmosphere is a very complex environment and strongly influenced by pollution from human activities. Air pollution, especially particulate, is one of the problematic of interest that requires regular monitoring. Atmospheric particulate matters are complex mixtures of substances suspended in the air. Their properties are defined according to their aerodynamic diameter. These particles may carry both essential elements to the life cycles and harmful contaminants (heavy metals, sulfur dioxide, etc.) [1]. So, this work aims to establish a Chemical characterization and origin of suspended atmospheric particles in Meknes city in Morocco.

2. Materials and methods

2.1. Sites and sampling campaigns

From March to October 2007, the sampling of atmospheric particulate matter with diameter less than or equal to 10 μm (PM-10) was carried out in the FAR Avenue (33,897439N, -5,536886W) (maps.google.fr) in the center of Meknes city (Hamriya), near a taxi station and not far from railway traffic. And, because of logistic reasons, the site was changed to an other similar site, in the Allal Ben Abdallah avenue (33,898881N, -5,546896W) (maps.google.fr) also in the center of Meknes city, from November 2007 to April 2008. This site is characterized also by dense road traffic and not far from railway traffic. The Figure 1 shows localization of sampling site in Meknes city. The samples of PM10 were carried out for a period of 24 hours once every six days to cover every day of the week



Figure 1. Map of location of sampling sites in the city of Meknes.

2.2. Sampling and analysis

The sampling was carried out using Gent sampler composed from two filters of polycarbonate placed in series allows to obtain a fine fraction with aerodynamic diameter lower or equalizes to 2.5 μm and coarse fraction with aerodynamic diameter between 2.5 μm and 10 μm [2-7]. In parallel, the samples were collected by Partisol 2000 (Thermo) equipped with PM-10 head. The used filters were in Teflon. The Gent filters have been attacked by 10 ml of nitric acid (HNO_3) accelerated by heating in the microwave oven ((Mars 5 CEM). The final solution was mixed with a standard solution of Se, before being analyzed by Total reflection X-Ray Fluorescence (TXRF) installed in *National Center for Energy, Sciences and Nuclear Techniques* (CNESTEN). The determined chemical elements are Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, and Zn. The analysis of Al was performed by Atomic Absorption Spectrometry (AAS) type SpectrAA 220 Varian also installed in CNESTEN. Elemental concentrations are expressed in (ng / Nm^3) to normal conditions of temperature and pressure. While two Partisol filters sampled in 2008 were used for the determination of lead isotope ratios. The analysis technique used is the Thermo-Ionization Mass spectrometry (TIMS). This is the spectrometer

Finnigan MAT 262 with solid source installed in *European Centre for Research and Teaching of Environmental Sciences* (CEREGE). The lead extraction procedure is well explained in Hamelin B. work (1990) [8].

2.3. Data processing tools: Enrichment Factor (EF)

The enrichment factor (EF) is a very interesting tool for comparing the contribution of anthropogenic sources in the natural mineral contribution. The EF is calculated as follows [9, 10] :

$$EF(Y)X = \frac{X_m/Y_m}{X_{ref}/Y_{ref}}, \quad (\text{Eq. 1})$$

where, X is the concentration of element which we want to determine the enrichment (from non-crustal sources), Y is the concentration of the reference crustal element (aluminum Al), m: measured in the sample, ref: reference in the area of continental crust. Other studies suggest, as reference element, Fe, Ti, Sc, Rb, Ba, Zr in addition to the Al [10-16]. However, Al is supposed to be purely crustal origin [17]. It is commonly accepted that $EF < 10$ of element means that it has a crustal origin. The $EF \gg 10$ suggests that the contribution of this element is came from another source (human activity, volcanoes, marine and biological), and finally the $EF \gg 500$ demonstrate a strong contribution of human activities [10, 16, 18].

3. Results and Discussion

3.1. Chemical compositions

The contents of 9 chemical components (Al, Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, Zn) measured by TXRF for fine and coarse fractions, as well as Al determined by AAS are expressed in ng/Nm^3 (at standard conditions for temperature and pressure).

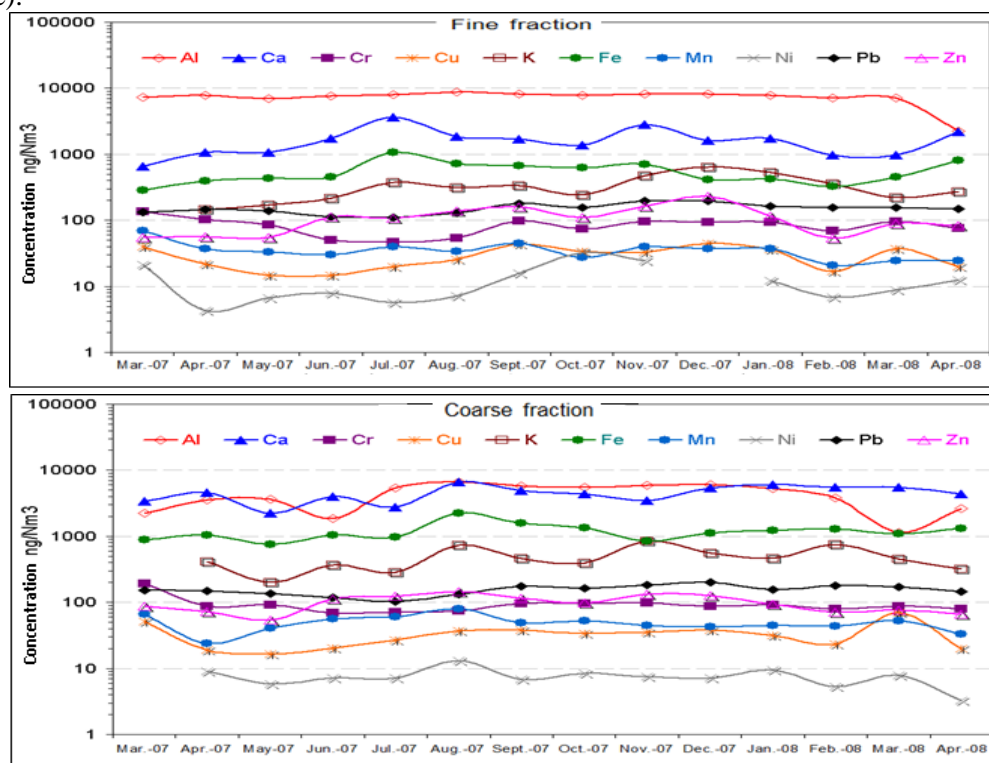


Figure 2. Monthly content of chemical compositions of fine and coarse fractions.

We present in Figure 2 monthly elementary developments contents for fine and coarse fractions. From this figure, the seasonal variation is not significant either for the fine fractions or coarse fractions. Furthermore, Al has the highest

concentrations ($11\,645\text{ ng / Nm}^3$) with abundance in the fine fractions, followed by Ca with average concentration of 6201 ng / Nm^3 and Fe with an average concentration of 1750 ng / Nm^3 , whereas, the Ni has the lowest levels (below 100 ng / Nm^3). The high measured levels reflect, in addition to terrigenous origin, presence of anthropogenic pollution, including the remobilization of road dust, the state fleet and fuel quality [19-22]. Against quality standards, particularly for regulated metals (Pb and Ni), the limit value of the European Directive and the WHO guideline value set at $500\text{ ng/m}^3/\text{year}$ [23-28] are respected for Pb where the average concentration was $310\text{ ng / Nm}^3/\text{year}$. Similarly, Moroccan standard ($2000\text{ ng/m}^3/\text{year}$) [29] is also respected. However, the quality target of $250\text{ ng/m}^3/\text{year}$ [23-26] is clearly exceeded. The average concentration of Ni ($20.5\text{ ng/Nm}^3/\text{year}$) is very close to the target value of the European Directive ($20\text{ ng/m}^3/\text{year}$) [24, 25, 26]. For other chemical components no standard exists currently.

3.2. Enrichment factors (EF)

The enrichment factors were calculated using Al as reference. In the lack of data on the soil of the Meknes region, we considered the average composition of the continental crust of the working *Squalli Houssaini A.S. (2007)* [30]. Thus, we present the seasonal variation of enrichment factors (EF) for chemical components (Ca, Cr, Cu, K, Fe, Mn, Ni, Pb, Zn) respectively determined in the case of continental crust [30] and in our study for fine and coarse fractions (Figure 3).

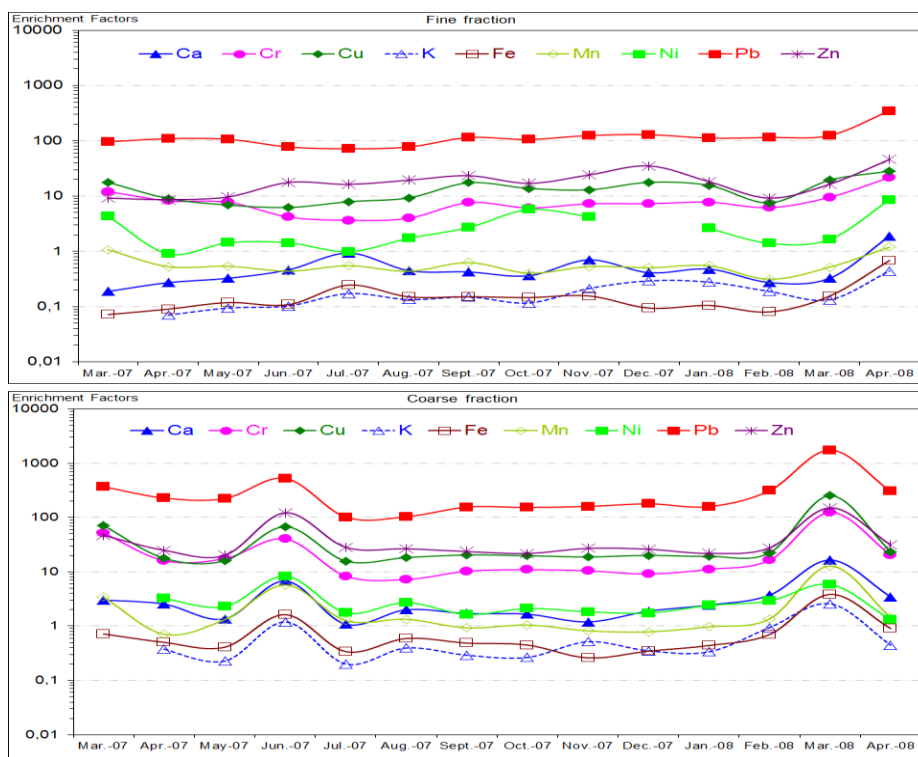


Figure 3. Seasonal variations of EF of fine and coarse fractions.

The enrichment factors for the elements (Ca, K, Fe, Mn, Ni) are very close to unity, indicating that the contents of these elements are similar to those in the reference site. So these elements can be natural. For other elements (Cr, Cu, Pb, Zn), high values of enrichment factors can be explained by the influence of anthropogenic sources or by a different chemical composition between urban and rural soil (reference) [30]. In addition, the enrichment in coarse fractions is more important than in fine fractions. Maximums Enrichment Factors observed in June 2007 and March 2008 in the case of coarse fractions are due to the low values of Al which are respectively of the order of 427 and 164 ng/Nm^3 .

To confirm obtained interpretations, we presented in Figures 4 and 5 the correlation diagram of enrichment factor for these chemical components (Cr, Cu, Pb, Zn) with Al concentrations for fine and coarse fractions. We note that the following elements (Cu and Zn) showed no correlation with Al, so we can conclude that these elements come from natural sources. Thus, the enrichment observed for Cu and Zn is not attributed to contamination of the soil, but perhaps due to a change of the nature of the soil. The other elements (Cr and Pb) correlated well with the Al indicating the influence of anthropogenic sources.

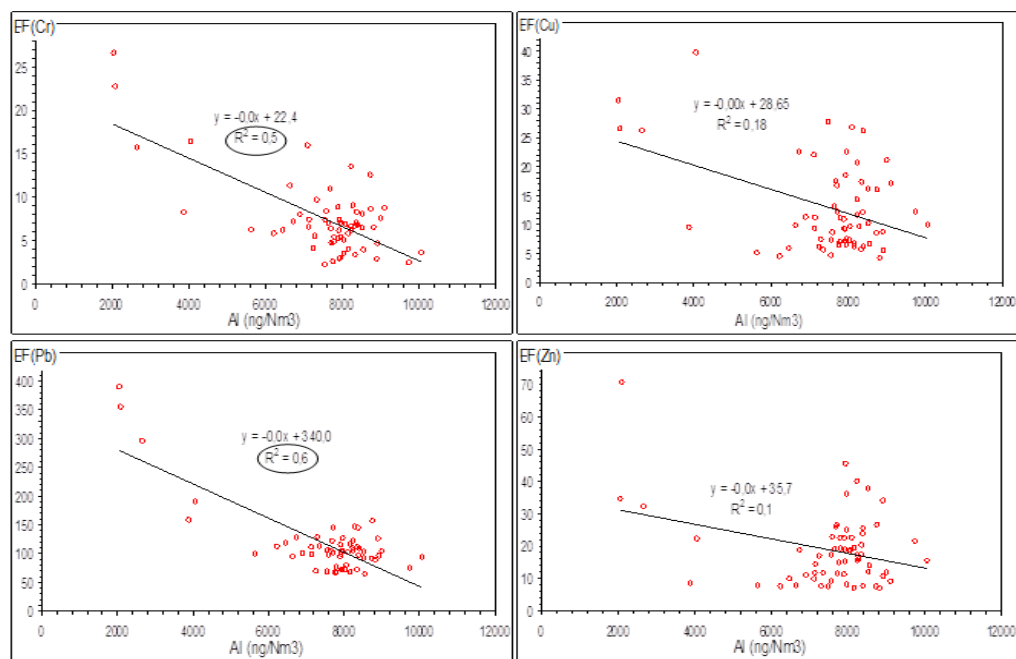


Figure 4. Correlation diagrams of enrichment factor based on the contents of Al in the finer fractions

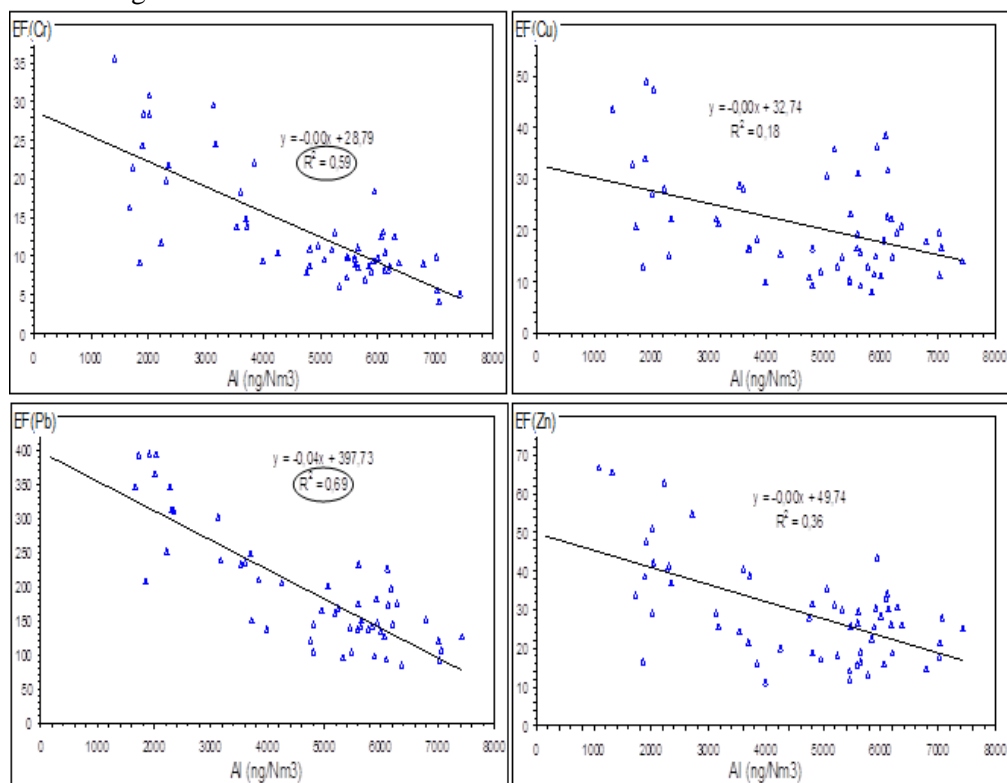


Figure 5. Correlation diagrams of enrichment factor based on the contents of Al in the coarse fractions.

3.3. Isotope ratios of lead

One of the advantages of lead for the study of the anthropogenic pollutants spread is the variety of its isotopic composition. The lead present in nature has four stable isotopes of atomic weights (204, 206, 207 and 208) [31]. The ratios of these isotopes are tracers of anthropogenic activity and sources of minerals [10]. The low abundance of the isotope 204 non-radiogenic does not allow precise measurements [10]. The knowledge of the isotopic composition of lead in a contaminated site, the composition of natural contribution in this site and the probable sources of anthropogenic contamination, allow determining the origin of the pollution [32]. Thus, and according to the results obtained concerning the anthropogenic lead and view its toxicity [33, 34], we calculated isotopic composition to better determine its origin and thus identify mixtures of sources from which it originated. The lead isotope ratios for PM10 collected on Partisol filters in 2008 are compared with fuels, urban aerosols and sediments characterize the geochemical background, Figure 6. Lead isotope ratios measured in the city of Meknes, has a signature belonging to the urban center. This is due to the presence of road traffic and the re-suspension of soil samples at the sampling sites in Meknes city. This result confirms the anthropogenic obtained when calculating the Enrichment Factor (EF) and determining the correlation diagram between Al and EF(Pb). Similarly, we note that the isotopic signatures of lead in our samples, collected at the road traffic, are in agreement with the results obtained in urban sites in several cities in China, Paris in France and Morocco.

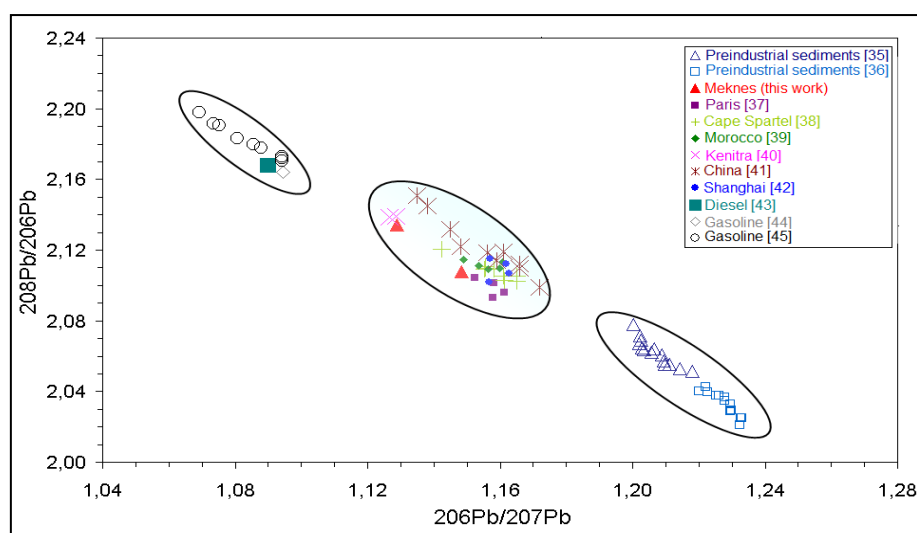


Figure 6. Isotope ratios $^{208}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$ of various area of atmospheric lead emissions: sediments, fuels and urban aerosols.

4. Conclusion

This work aims to develop a better understanding of the air quality in the city of Meknes. Chemical characterization of the particulate matter was conducted between 2007 and 2008 in urban areas where traffic is dense. The majority of chemical compositions obtained shows the same distribution for fine and coarse fractions and generally do not show a great seasonal variability, with high levels compared to European and Moroccan standards; especially for Pb and Ni. Calculating the Enrichment Factor allows identification of natural sources of pollution for Ca, Cu, Fe, K, Mn, Ni and Zn and source of anthropogenic pollution for Cr and Pb. A confirmation of results obtained in the lead case was provided by the study of isotopic signature.

Acknowledgments-This study was conducted with the support of French-Moroccan program VOLUBILIS (AI MA / 05/129). We thank all the people that have agreed to help us at various levels to sampling campaigns.

References

- [1] J.P. Quisefit, A. Gaudichet, *Anal. Mag.*, 26(9) (1998) M21-M27.
- [2] B.A. Begum, E. Kim, S.K. Biswas, P.K. Hopke, *Atmos. Environ.*, 38 (2004) 3025-3038.
- [3] B.A. Begum, S.K. Biswas, E. Kim, P.K. Hopke, M. Khaliquzzaman, *J. Air Waste Manag. Assoc.*, 55 (2005) 227-240.
- [4] B.A. Begum, S.K. Biswas, P.K. Hopke, D.D. Cohen, *Aerosol Air Qual. Res.* 6(4) (2006) 334-359.
- [5] R. Hitzenberger, A. Berner, Z. Galambos, W. Maenhaut, J. Cafmeyer, J. Schawarz, K. Müller, G. Spindler, W. Wiprecht, K. Acker, R. Hillamo, T. Mäkelä, *Atmos. Environ.*, 38 (2004) 6467-6476.
- [6] I. Salma, M. Dal Maso, M. Kulmala, G. Zárny, *Microchem. J.*, 73 (2002) 19-26.
- [7] G. Zárny, M. Óvári, I. Salma, I. Steffan, M. Zeiner, S. Caroli, *Microchem. J.*, 76(90) (2004) 31-34.
- [8] B. Hamelin F. Grousset, E.R. Sholkovitz, *Geochim. Cosmochim. Acta*, 54 (1990) 37-47.
- [9] N. Guvenç O. Alagha, G. Tuncel, *Environ. Inter.*, 29(2003) 631-640.
- [10] S. Veschambre, *PhD Thesis, University of Pyrenees*, (2006) 444 p.
- [11] S. Azimi, *PhD Thesis, National School of Bridges and Roads*, (2004) 275p.
- [12] L. Bergamaschi, E. Rizzio, G. Giaveri, A. Profumo, S. Loppi, M. Gallorini, *Chemosphere*, 55 (2004) 933-939.
- [13] J. Carignan, A. Simonetti, C. Gariepy, *Atmos. Environ.*, 36 (2002) 3759-3766.
- [14] L. Leleyter, F. Baraud, *Geoscience Report*, 37 (2005) 571-579.
- [15] S. Roy, P. Negrel, *Sci. Total Environ.*, 277 (2001) 225-239.
- [16] A. Veyseyre, K. Moutard, C. Ferrari, K. Van De Velde, C. Barbante, G. Cozzi, G. Capodaglio, C. Boutron, *Atmos. Environ.*, 35 (2001) 415-425.
- [17] D. Baque, *PhD Thesis, University of Toulouse III – Paul Sabatier*, (2006) 482 p.
- [18] A. Simonetti, C. Gariepy, J. Carignan, L. Poissant, *J. Geophysical Res.*, 105 (2000) 12263-12278.
- [19] R.M. Harrison, R. Tilling, R.M.S. Callen, S. Harrad, K. Jarvis, *Atmos. Environ.*, 37 (2003) 2391-2402.
- [20] C.C. Lin, S.J. Chen, K.L. Huang, W.I. Hwang, G.P. Chang-Chien, W.Y. Lin, *Environ. Sci. Technology*, 39(21) (2005) 8113-8122.
- [21] G. Weckwerth, *Atmos Environ*, 35 (2001) 5525-5536.
- [22] P. Wahlin, R. Berkowicz, F. Palmgren, *Atmos. Environ.*, 40 (2006) 2151-2159.
- [23] Airfobep, *Mesure des niveaux moyens de dioxyde de soufre de la région de l'ouest des Bouches-du-Rhône*, (2003) 36 p.
- [24] Airfobep, *La qualité de l'air en région Midi-Pyrénées. Annual Report*, (2008) 72 p.
- [25] JOUE, *Official Journal of the European Union*, N° 23 (2005) 3-16.
- [26] Oramip, *La qualité de l'air en Midi-Pyrénées. Activity Report*, (2010) 78 p.
- [27] C. Elichegaray, S. Bouallala, J. Colosio, H. Desqueyroux, L. Galsomies, H. Pernin, N. Poisson, R. Stroebe, *La qualité de l'air en France - tendances et perspectives. ADEME/Department of monitoring air quality*, (2003) 16 p.
- [28] WHO, *Guidelines for air quality*, Geneva, (2000).
- [29] MATEE, *Ministry of Spatial Planning, Water and Environment, State Secretariat of Environment Officer. Air Service & National Laboratory of Environment, Directorate of Monitoring and Risk Prevention*, (2003) 45p.

- [30] A.S. Squalli Houssaini, H. Messaouri, I. Nasri, M.P. Roth, C. Nejari, M.N. Benchekroun, *Inter. J. Environ. Health Res.*, 17(4) (2007) 243-257.
- [31] C. Lefevre, *geochronology courses, University of Sciences et Technologies in Lille*, (2009) 25 p.
- [32] F. Arnaud, *PhD Thesis, University of Sciences and Techniques in Lille*, (2004) 196 p.
- [33] M.A. Oliver, *Eur.J. Soil Sci.*, 48 (1997) 573-592.
- [34] J. Rodier, *L'analyse de l'eau : eaux naturelles, eaux résiduaires, eaux de mer. 7th edition, Dunod, Paris* (1984).
- [35] S-S. Sun, *The Philosophical Transactions of the Royal Society, London, Série A*, 297 (1980) 409-445.
- [36] W.M. White, B. Dupre, P. Vidal, *Geochim. Cosmochim. Acta*, 49 (1985) 1875-1886.
- [37] D. Widory, S. Roy, Y. Le Moullec, G. Goupil, A. Cocherie, C. Guerrot, *Atmos. Environ.*, 38 (2004) 953-961
- [38] J. Miralle, *PhD Thesis, Geochemistry. University of Law, Economics and Science - Aix-Marseille III*, (2004).
- [39] L. Alleman, *PhD Thesis, University Aix-Marseille III*, (1997) 291 p.
- [40] M. Zghaid, *PhD Thesis, University Moulay Ismail in Meknes*, (ongoing thesis).
- [41] C.S.C. Wong, X.D. Li, G. Zhang, S.H. Qi, X.Z. Peng, *Atmos. Environ.*, 37 (2003) 767-776.
- [42] J. Zheng, M. Tan, Y. Shibata, A. Tanaka, Y. Li, G. Zhang, Y. Zhang, Z. Shan, *Atmos. Environ.*, 38 (2004) 1191-1200.
- [43] M.L. Geagea, P. G-L.F. Stille, M. Millet, *Environ. Sci. Technology*, 42 (2008) 692-698.
- [44] C. Cloquet, J. Carignan, G. Libourel, T. Sterckeman, E. Perdrix, *Environ. Sci. Technology*, 40 (2006) 6594-6600.
- [45] F. Monna, J. Lancelot, I.W. Croudace, A.B. Cundy, J.T. Lewis, *Environ. Sci. Technology*, 31(8) (1997) 2277-2286