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Trace Elemental Composition in PM₁₀ and PM_{2.5} Collected in Cardiff, Wales

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Abstract

A Dichotomous Sampler Model 241 was used to collect PM₁₀ and PM_{2.5} samples, from midnight to midnight on every other day, from December 2009 to December 2010. Ca, K, Mg, Na, Al, Pb, Cr, Ni, Zn, Cu, Cd, and Fe were determined by Atomic absorption Spectrometer (AAS). The mass concentration ranged from 18.0 to 83.3 µg/m³, with an annual average of 37.9 µg/m³ for PM₁₀. The mass concentration of PM_{2.5} ranged from 3.0 to 36.0 µg/m³ with an annual average of 14.1 µg/m³. Most of the elements in both PM fractions were abundant in the winter season. A good correlation was observed between PM₁₀ and PM_{2.5}. Enrichment factors (EF) for elements in PM₁₀ and PM_{2.5} were calculated and indicate that elements from anthropogenic origins such as Zn, Pb, Cu, Cr and Cd were highly enriched with respect to crustal elements Al, Fe and Ca.

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Keywords:

1. Introduction

Atmospheric pollution is a major public concern in urban areas because a number of studies have shown an association between pollution levels and health outcomes. Particulate matter, PM, is considered one of the most hazardous pollutants to human health [1]. PM₁₀ and, in particular, fine particles PM_{2.5} on inhalation are capable to reach conductive airways of the tracheo-bronchial tree [2, 3]. There are associations between fine particles and a.

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A number of health conditions, including asthma, bronchitis, acute and chronic respiratory symptoms, even at low concentrations [4,5,6]. Short-term effects of exposure to PM₁₀ and PM_{2.5} have been noted on several health outcomes: infant mortality [7], adult mortality [8], incidence of stroke [9] and hospital admissions for cardiovascular diseases, especially among sensitive sub-groups of population such as patients with diabetes and chronic obstructive pulmonary disease [10,11]. The main sources for ambient PM at urban roadways are vehicle exhausts, emissions from tyre and brake wear and re-suspension of road dust [12]. Element aerosols in the urban ambient atmosphere are produced by various anthropogenic and natural sources. Anthropogenic sources include combustion of fossil fuels and wood, exhaust emission from vehicles, industrial activities, energy production, construction activities and waste incineration, while natural sources include volcanic activity, wind eroded soil dusts, forest fires, and sea salt spray [13, 14,15]. Elements associated with PM can be grouped into two major groups: earth crust elements or soil tracers, such as Ca, K, Mg, Na, Al and Fe or anthropogenic tracers, such as Pb, Cr, Ni, Zn, Cu and Cd. The objectives of the study are to:

- (1) Determine levels in PM₁₀ and PM_{2.5} in Cardiff,
- (2) Characterize the trace elements composition Ca, K, Mg, Na, Al, Pb, Cr, Ni, Zn, Cu, Cd, and Fe, and
- (3) Identify the sources of the trace elements in the PM fractions.

2. Methods

2.1 Sampling Site.

Cardiff is the capital city and most populous county of Wales, UK, with a population of over 300,000. The 24-h, midnight to midnight, PM₁₀ and PM_{2.5} sampled using a Dichotomous sampler during the period from December 2009 to December 2010 at an urban site. The monitoring site was located in Cardiff urban area, N38°14.785'; E21°44.180, in a commercial, residential and industrial area. The Dichotomous sampler was located on the second floor about 8m above ground level.

2.2. Sample Collection

Four sampling periods from December 2009 to December 2010 were identified to represent winter, spring, summer and autumn. Particulate samples were collected using Dichotomous Sampler Model 241, which consists of an Omni-directional aerosol inlet, a virtual impactor assembly, two 37mm filter holders and a tripod mount. The dichotomous sampler 37 mm diameter dual-filter samples simultaneously PM_{2.5} and coarse PM₁₀. A total of 366 PM_{2.5} and PM₁₀ samples were collected

Background contamination was determined by using operational blanks (unexposed filters), which were processed along with field samples. Filters were conditioned in a desiccator for twenty-four hours, before and after exposure, and then weighed on an electronic microbalance in a temperature and relative humidity controlled environment to determine PM. Each filter was weighed three times, and the net PM was obtained by subtracting the pre-sampling weights from the post-sampling weights

2.3 Extraction Procedure and Analysis

During the extraction of metals, each filter was cut into two. The analytical procedures for determination of trace metals in filters described in Work Assignment 5-03[16] and SOP MLD061 [17] were followed. Exposed and blank filters were extracted in Teflon centrifuge tubes containing 25 ml of 4% nitric acid followed by ultrasonic treatment for 3 hours using sonication bath heated to 69°C. After sonication, samples were allowed to cool down to room temperature. The samples were then filtered through a 0.22µm pore size filter and deionised water added to make up to a volume of 50 ml. Atomic Absorption Spectrometer (SOLAAR 969) used to analyse for Ca, K, Mg, Na, Al, Pb,

Cr, Ni, Zn, Cu, Cd, and Fe. For calibration, standard solutions containing all metals of interest were prepared using Merck certified atomic absorption stock standard solutions.

3.0 Results and discussion

3.1. Mass Concentrations

The PM was obtained by subtracting the pre-sampling weights from the post-sampling weights. The annual average concentrations of PM10 and PM2.5 were $37.9 \pm 11.7 \mu\text{g}/\text{m}^3$ and $14.1 \pm 5.9 \mu\text{g}/\text{m}^3$, respectively and did not exceed the set limits in the air quality standard regulations 2010. These levels are below the 2005 EU annual standard of $40 \mu\text{g}/\text{m}^3$ for PM10 [18] and below the EU annual PM2.5 limit value of $25 \mu\text{g}/\text{m}^3$ which is to be met by 2020[19].

The mean values of PM mass concentrations in some urban areas of European countries are shown in Table 1. Comparing these data to the mass concentrations values of both the coarse PM10 and PM2.5 obtained from urban Cardiff, shows that the results were within observed PM levels for the region.

PM10 and PM2.5 mass concentrations for different seasons at Cardiff are shown in Figure 1. The average concentrations of PM10 was $39.7 \pm 13.0 \mu\text{g}/\text{m}^3$ in winter, $34.6 \pm 7.6 \mu\text{g}/\text{m}^3$ in spring, $39.0 \pm 13.0 \mu\text{g}/\text{m}^3$ in summer and $38.4 \pm 11.1 \mu\text{g}/\text{m}^3$ in autumn, respectively. While the seasonal average concentration of PM2.5 was $14.9 \pm 6.6 \mu\text{g}/\text{m}^3$ in winter, $13.1 \pm 4.2 \mu\text{g}/\text{m}^3$ in spring, $14.0 \pm 6.56 \mu\text{g}/\text{m}^3$ in summer and $14.0 \pm 4.8 \mu\text{g}/\text{m}^3$ in autumn, respectively.

Table 1. PM mass concentrations in local and European cities ($\mu\text{g}/\text{m}^3$)

| Source | PM10 ($\mu\text{g}/\text{m}^3$) | PM2.5($\mu\text{g}/\text{m}^3$) |
|---------------------------------|-----------------------------------|-----------------------------------|
| Athens,Greece[20] | 75 | N.D. |
| Barcelona,Spain[21] | 48 | 33 |
| Belgrade [22] | 68 | 61.4 |
| Melpitz , Germany [23] | 22 | 17 |
| Birmingham,UK [24] | N.D. | 17 |
| Haarlemmerweg, Netherlands [25] | 27.5 | 17.8 |

N.D. = No Data

Over the four seasons, average concentrations of PM10 and PM2.5 were highest in winter and lowest in spring, although there was only a small seasonal variation over the period. During winter, PM fractions usually became trapped near the ground level due to lower mixing height as a result of low temperature [26]. Also, the concentrations of PM may increase due to additional PM sources such as higher traffic, cold start of engines, domestic heating [27], or perhaps due to meteorological conditions [28].

Figure 2 (a) and (b) presents a wind-rose diagram for the winter and spring seasons (2009–2010), respectively. During the winter, the air masses flowed more frequently from the west (W) and from the west-north west (WNW) with a maximum speed of more than 11 m/s. As is shown, no prevailing direction and calm conditions favoured in the study area for 1% of the time during winter. As a result, the highest concentrations of PM10 and PM2.5 were observed during the winter months (December, January and February). Pollutants can be trapped by this condition and delay their dispersion and allowed the accumulation of particulate emitted locally [29].

The relative contribution of fine and coarse particles can be assessed by looking at PM2.5/PM10 ratios. The annual PM2.5/PM10 ratio varied from 0.17 to 0.43 with a mean of 0.37, which indicates that PM10 contributed a large portion to the PM content in the studied area. High ratios of PM2.5/PM10 are attributed to vehicle emissions

and secondary particles formed in the atmosphere from gases [30], while smaller ratios are related to strong dust emissions and re-suspension due to high traffic volume [31].

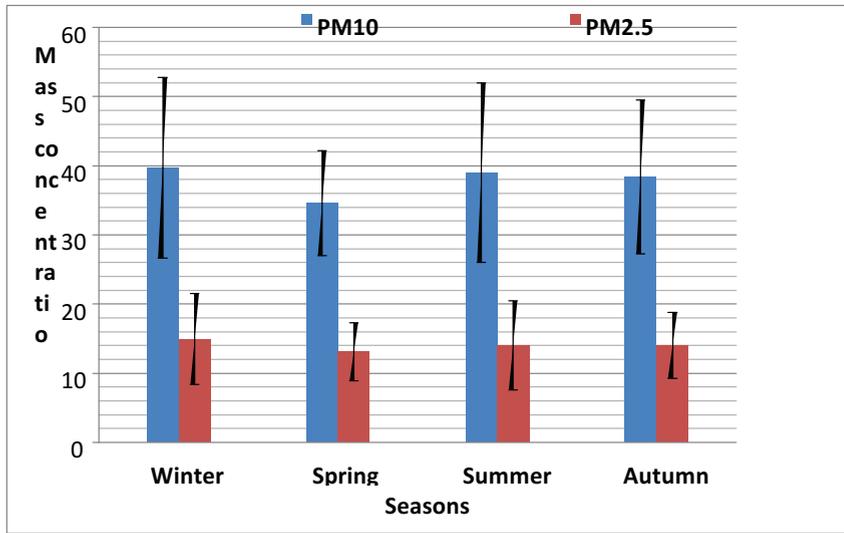


Figure 1. Seasonal variation of PM10 and PM2.5 mass concentrations with standard error bars

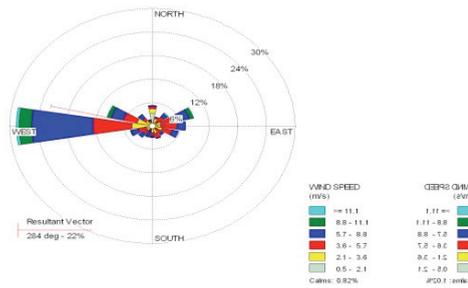


Figure 2a. Winter wind rose, 2009–2010

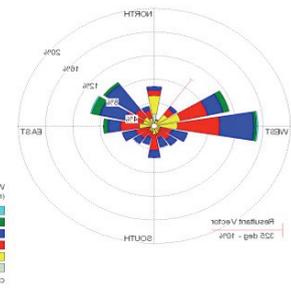


Figure 2b. Spring wind rose, 2009–2010

Figure 3 shows the scatter plots of PM10 and PM2.5 which indicates that these two parameters are highly related, $r^2=0.7$, to one another in a linear relationship ,

$$PM2.5 = 0.43[PM10] - 2.12. \tag{1}$$

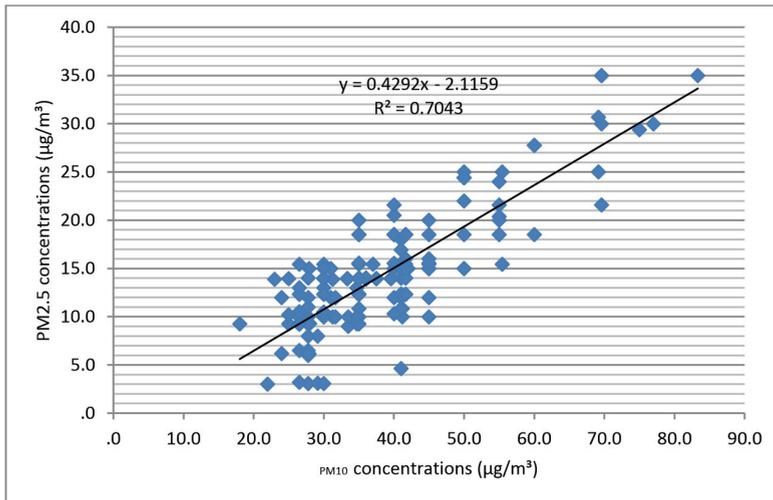


Figure 3. Scatter plots of PM2.5 concentration against PM10 concentration ($\mu\text{g}/\text{m}^3$)

3.2 Elemental Concentrations

Twelve metals were analyzed in PM10 and PM2.5 samples: Ca, K, Mg, Na, Al, Pb, Cr, Ni, Zn, Cu, Cd, and Fe. The concentrations of these elements varied in the PM10 and PM2.5, there was also a variation over the four seasons. Of the twelve elements analyzed, in both PM10 and PM2.5, K, Na, Cr and Fe were observed to be highest in summer, while Ca, Al, Pb and Cd recorded highest values in Spring. Cu and Ni highest values were recorded in summer and Zn and Mg highest values noted in autumn. From the study, the total sums of toxic and crust metals were highest in winter compared to the other seasons, while a combined sum of crust and anthropogenic metals were lowest in summer. On an annual basis, PM10 and PM2.5 concentrations of crustal elements were higher than the anthropogenic elements. Zn was the most abundant anthropogenic element and was followed by Cu and Pb, while Fe, K and Ca were the most abundant crustal elements. It was observed that Fe, K, Ca, Na and Al were the most abundant elements in all PM10 and PM2.5, and the sum of these five elements accounts for 93% and 91% in the total elemental composition in PM10 and PM2.5 respectively.

3.3 Sources of Trace Elements

Enrichment factor (EF) is one approach that has been used to differentiate between the metals originating from anthropogenic activities and those from natural procedure, and to understand the chemistry of PM [32,33]. The enrichment factor for any element X relative to control/unpolluted references material is defined by

$$\text{EF crust, x} = (X / Y)_{\text{air}} / (X / Y)_{\text{control}}, \quad (2)$$

Where EF crust, x is the enrichment factor of X, Y is a reference element for crustal material $(X / Y)_{\text{air}}$ is the concentration ratio of X to Y in the aerosol sample, and $(X / Y)_{\text{control}}$ is the average concentration ratio of X to Y in control/unpolluted references (crust) material.

Elements such as Al, Si, Ti, Fe are commonly used as a point of reference for the calculation of factors, because they are very abundant in crustal material and are not significantly affected by pollution [34]. The EF for each metal in PM10 and PM2.5 samples were calculated as shown in Figure 4, using the aluminium (Al) as reference element in this study, based on the average elemental concentration data of the upper continental crust [35]. Six contamination categories of EF are recognized, which are increasing with contribution of the anthropogenic origins: < 1

background concentration, 1- 2 depletion to minimal enrichment, 2 – 5 moderate enrichment, 5 – 20 significant enrichment, 20 – 40 very high enrichment and > 40 extremely high enrichment.

According to the degree of enrichment, the studied elements were grouped as follows. As Figure 7 shows, Zn exhibits the highest enrichment factor (>1,000). Pb and Cu also show high enrichment factors (>40), indicating that concentration of these elements in particles is enriched by sources that are not of crustal origin, such as combustion of fossil hydrocarbons, vehicular traffic and emissions of metal-working industries [36]. Cr, Cd, Fe and K appear to be between significant and moderate enrichment. Other elements, such as Mg, Ni, Na and Ca, were shown to have low enrichment factors in PM10 and PM2.5 particles. Most of the crustal components showed smaller values of EF. Low EF values for crustal components were also observed by [37] in a study of field measurements of PM10 conducted in urban locations.

Enrichment factors are also higher in PM2.5 samples than in PM10, showing that the inhalable particulate matter fraction is enriched in elements such as Pb, Cu, Cr and Cd, which are of health-concern. The high enrichment of these elements (Zn, Pb, Cu, Cr, Cd) in urban Cardiff suggests that the dominant sources for these elements are non-crustal, i.e. a variety of pollution emissions, such as vehicles activities (brakes, oil combustion, exhaust emissions, rubber tyres), and mechanical erosion of metallic surfaces. The values of enrichment factors, in urban Cardiff, follow the sequence: Zn > Pb > Cu > Cr > Cd > Fe > K > Ca > Na > Ni > Mg > Al.

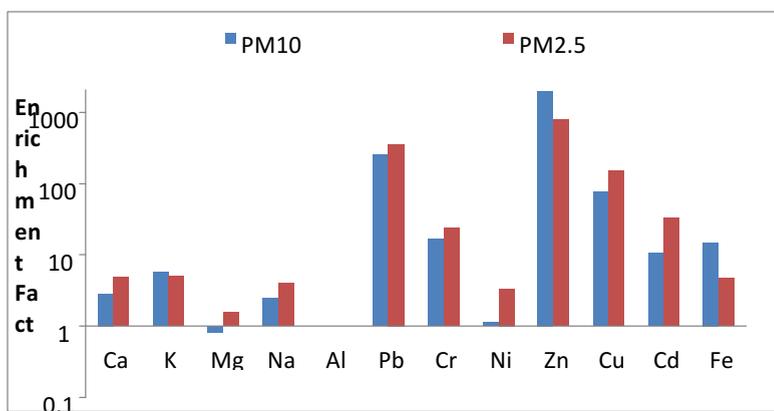


Figure 4 . Enrichment factors of elements in PM10 and PM2.5

4 Conclusion

The contributions of this study to the science of particulate and gaseous pollutant in urban area include profiling the seasonal means of the mass concentrations of pollutants PM10 and PM2.5 including the interaction between these pollutants in urban Cardiff. This has not been recently undertaken in Cardiff. PM2.5 measurements are rarely determined for a considerable length of time as done in this study and this is one of the very few studies that has determined the mass and chemical concentrations of PM2.5 in urban environments.

Developments of a suitable and appropriate method to analyze anions, cations and elements for PM samples in Cardiff resulted in chemical analysis of the PM10 and PM2.5. Major chemical pollutants in the area identified included cations (Ca^{2+} , Mg^{2+} , K^{+} , Na^{+}), crustal elements (Ca, K, Mg, Na, Al, Fe) and trace metals (Pb, Cr, Ni, Zn, Cu, Cd). Profiles of the crustal elements among the measured elements in PM10 and PM2.5 in urban Cardiff, determination of enrichment factors for the measured elements in PM10 and PM2.5 in urban Cardiff and evaluation of annual and seasonal variations of PM2.5/PM10 ratios in urban Cardiff are significant contribution to pollution science. An evaluation of how meteorological parameters affect annual and seasonal variations of PM10 and PM2.5

was completed

In the present study the concentrations of Ca, K, Mg, Na, Al, Pb, Cr, Ni, Zn, Cu, Cd, and Fe in PM₁₀ and PM_{2.5} particles were determined in an urban area in Cardiff, during the period December 2009 - December 2010. The annual average concentration of PM₁₀ (37.9 µg/m³) and PM (14.1 µg/m³) did not exceed the EU proposed annual limit value of 40 and 25 µg/m³ for the PM₁₀ and PM_{2.5}, respectively. The PM levels were highest in winter. The annual ratios of fine particle (PM_{2.5}) / coarse particle (PM₁₀) were averaged 0.40, indicating that there was enrichment in coarse particulates during the different monitoring seasons. The concentrations of elements such as Zn, Pb, Cu, Cr and Cd had high EF values, suggesting their origins were from vehicles activities (brakes, oil combustion, exhaust emissions, wheels rubber) and soil dust sources.

References

- [1] WHO, Health risk of particulate matter from long-range transboundary air pollution. Joint WHO/Convention Task Force on the health aspects of air pollution. Denmark: World Health Organization Europe, Publication E88189; 2006.
- [2] Duhme, H, Weiland, SK, Keil, U. Epidemiological Analyses of the Relationship between Environmental Pollution and Asthma. *Toxicol Lett* 1998; 102–103:307–316.
- [3] Harrison, R, Yin, J. Particulate matter in the atmosphere: which particle properties are important for its effect on health. *Sci Total Environ* 2000; 249: 85–101.
- [4] Pope CA III, Burnett RT, Thun MJ, Calle EE, Krewski D, Ito K, Thurston GD. Lung Cancer, Cardiopulmonary Mortality, and Long-Term Exposure to Fine Particulate Air Pollution. *J Am Med Assoc* 2002; 287: 1132–1141.
- [5] Akoto O, Ephraim JH, Darko G. Heavy metals pollution in surface soils in the vicinity of abundant railway servicing workshop in Kumasi, Ghana. *Int J Environ Res* 2008; 2 (4):359-364.
- [6] Farina F, Sancini, G, Battaqlia C, Tinaqlia V, Mantecca P, Camatini M, Palestini P. Milano Summer Particulate Matter (PM₁₀) Triggers Lung Inflammation and Extra Pulmonary Adverse Events in Mice. *PLOS One* 2013; 8(2):e56636.
- [7] Hajat S, Armstrong B, Wilkinson P, Busby A, Dolk H. Outdoor air pollution and infant mortality: analysis of daily time-series data in 10 English cities. *J Epidemiol Community Health* 200; Aug 61(8):719-22.
- [8] Ostro B, Feng WY, Broadwin R, Green S, Lipsett M. The effects of components of fine particulate air pollution on mortality in California: results from CALFINE. *Environ Health Perspect* 2007; Jan: 115(1):13-9
- [9] Kettunen J, Lanki T, Tiittanen P, Aalto PP, Koskentalo T, Kulmala M, Salomaa V, Pekkanen JL. Associations of fine and ultrafine particulate air pollution with stroke mortality in an area of low air pollution levels. *Stroke* 2007; Mar 38(3):918-22.
- [10] Peel JL, Metzger KB, Klein M, Flanders, WD., Mulholland, JA, Tolbert, PE. Ambient air pollution and cardiovascular emergency department visits in potentially sensitive groups. *Am J Epidemiol* 2007; Mar 15; 165(6):625-33.
- [11] Atkinson RW, Carey JM, Kent, AJ, van Staa TP, Anderson H, Cook, DG. Long-term exposure to outdoor air pollution and incidence of cardiovascular diseases. *Epidemiology* 2013; 24(1): 44-53.
- [12] Bathmanabhan S, Madanayak, S. Analysis and interpretation of particulate matter – PM₁₀, PM_{2.5} and PM₁ emissions from the heterogeneous traffic near an urban roadway. *Atmospheric Pollution Research* 2010; 184–194.
- [13] Allen AG, Nemitz E, Shi JP, Harrison RM, Greenwood JC. Size distributions of trace metals in atmospheric aerosols in the United Kingdom. *Atmospheric Environment* 2001; 35(27):4581–4591.
- [14] Bilos C, Colombo JC, Skorupka CN, Presa MJR. Sources, distribution and variability of airborne trace metals in La Plata City area, Argentina. *Environmental Pollution* 2001; 111(1): 149–158.
- [15] Wang X., Sato T, Xing B S, Tamamura S, Tao S. Source identification, size distribution and indicator screening of airborne trace metals in Kanazawa, Japan. *Journal of Aerosol Science* 2005; 36(2):197–210.
- [16] Environmental Protection Agency (EPA) Standard Operating Procedure for the Determination of Metals in Ambient Particulates Matter Analyzed by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS). Work Assignment 5-03. U.S; 2005
- [17] Air Resources Board (ARB) Standard Operating Procedure (SOP) for the Trace Elemental Analysis of Low-volume Sample Using Inductively Coupled Plasma-Mass Spectrometry (ICP/MS). California Environ Protection Agency, SOP MLD06; 2002.
- [18] EC, European Commission, DG Environment. Working Group on Arsenic, Cadmium and Nickel Compounds Ambient Air Pollution by As, Cd and Ni compounds-Position Paper. Office for Official Publications of the European Communities, Luxembourg; 2001
- [19] Harrison R Yin J. Characterisation of particulate matter in the United Kingdom. Report produced for Defra, the National Assembly for Wales, the Department of the Environment in Northern Ireland and the Scottish Executive. The University of Birmingham; 2004
- [20] Valavanidis V, Fiotakis K, Vlahogianni T, Bakeas EB, Triantafyllaki S, Paraskevopoulou V, Dassenakis M. Characterization of atmospheric particulates, particle-bound transition metals and polycyclic aromatic hydrocarbons of urban air in the centre of Athens (Greece) .*Chemosphere* 2006; 65:760–768.
- [21] Pérez N, Pey J, Querol X, Alastuey A, López M, Viana M. Partitioning of major and trace components in PM₁₀–PM_{2.5}–PM₁ at an urban site in Southern Europe. *Atmos Environ* 2007; 42(8): 1677–1691.
- [22] Tasic M, Rajsic S, Novakovic V, Mijic Z. An assessment of air quality in Belgrade urban area: PM₁₀, PM_{2.5} and trace metals. *J Phys Conf Ser* 2007; 71: 012016.

- [23] Spindler G , Brüggemann E, Gnauk T, Grüner A, Müller K, Herrmann, H. A four-year size-segregated characterization study of particles PM10, PM2.5 and PM1 depending on air mass origin at Melpitz. *Atmos Environ* 2010; 44(2):164–173.
- [24] De Miguel E, Llamas JF, Chacón E, Berg T , Larssen S, Røyset O, Vadset, M. Pollution measurement. *Atmos Environ* 1997; 31:2733-2740.
- [25] Boogaard H, Kos GPA, Weijers EP, Janssen NAH, Fischer PH, Zee S, Hartog JJ, Hoek G. Contrast in air pollution components between major streets and background locations: particulate matter mass, black carbon, elemental composition, nitrogen oxide, and ultrafine particle number, *Atmos Environ* 2011;45: 650–658.
- [27] Tsitouridou R , Voutsas D, Kouimtzis, T. Ionic composition of PM10 in the area of Thessaloniki, Greece. *Chemosphere* 2003;52:pp. 883–891.
- [28] Grivas, G, Chaloulakou A, Samara C, Spyrellis N. Spatial and temporal variation of PM10 mass concentrations within the Greater Area of Athens, Greece. *Water Air Soil Poll* 2004; 158(1): 357–371.
- [29] Intergovernmental Panel on Climate Change (IPCC), *Climate Change*. Cambridge University Press, New York; 2009.
- [30] Evagelopoulos V, Zoras S, Triantafyllou AG, Albanis TA. PM10-PM2.5 Time Series and Fractal Analysis. *Global NEST Journal* 2006; 8:234-240.
- [31] Environmental Protection Agency (EPA), *Criteria Document on Particulate Matter*, draft report; 2001
- [32] Lee S, Liu W, Wang Y, Russell AG, Edgerton ES. Source apportionment of 634 PM2.5: Comparing PMF and CMB results for four ambient monitoring sites in the 635 south-eastern United States. *Atmos Environ* 2008; doi: 10.1016.
- [33] Olubunmi FE Olorunsola OE. Evaluation of the status of heavy metal pollution of sediment of Agbabu bitumen deposits area, Nigeria. *Eur J Sci Res* 2010; 41(3):373–382.
- [34] Herrera, MJ and Rojas MJ. Concentration of PM10 in the Metropolitan Area of Costa Rica, Central America: Chemical composition and potential sources. *Atmósfera* 2010; 23(4):307-323.
- [35] Taylor SR, McLennan SM. *The Continental Crust: its Composition and Evolution*. Blackwell Scientific Publications, Oxford; 1985.
- [36] Janssen NAH, Van Mansom DFM, Van Der Jagt K, Harseema H, Hoek G. Mass concentration and elemental composition of airborne particulate matter at street and background locations. *Atmos Environ* 1997; 31(8):1185–993.
- [37] Cao JJ, Shen ZX, Chow JC, Qi, GW, Watson JG. Seasonal variations and sources of mass and chemical composition for PM10 aerosol in Hangzhou, China. *Particuology* 2009; 7: 161–168.