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Levels of selected metals in ambient air PM10 in an urban site of Zaragoza (Spain)

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Abstract

An assessment of the air quality of Zaragoza (Spain) was performed by determining the trace element content in airborne PM10 in a sampling campaign from July 2001 to July 2002. Samples were collected in a heavy traffic area with a high volume air sampler provided with a PM10 cutoff inlet. The levels of 16 elements (Al, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V, and Zn) were quantified after collecting the PM10 on Teflon-coated glass fiber filters (GFF). Regarding the PM10, 32% exceedance of the proposed PM10 daily limit was obtained, some of them corresponding to summer and autumn periods. The limit values of toxic trace elements from US-EPA, WHO, and EC were not exceeded, considering Zaragoza as a moderately polluted city under the current air quality guidelines. The contribution of anthropogenic sources to atmospheric elemental levels was reflected by the high values of enrichment factors for Zn, Pb, and Cu compared to the average crustal composition. Statistical analyses also determined the contribution of different sources to the PM10, finding that vehicle traffic and anthropogenic emissions related to combustion and industrial processes were the main pollutant sources as well as natural sources associated with transport of dust from Africa for specific dates. Regarding the influence of meteorological conditions on PM10 and trace elements concentrations, it was found that calm weather conditions with low wind speed favor the PM10 collection and the pollution for trace elements, suggesting the influence of local sources.

Keywords: Trace elements; Urban air; Pollution sources; PM10; Statistical analyses

1. Introduction

According to the WHO, 4–8% of deaths occurring annually in the world are related to air pollution (Kathuria, 2002). The main pollution sources are associated with anthropogenic activities.

In most countries, policies of these emissions have been and/or are being established with the aim of facing environmental pollution. One of the pollutants currently legislated in the European Union is the particulate matter of an aerodynamic size less than 10 μm in diameter (PM10), with a 24-h limit of 50 $\mu g/m^3$, not to be exceeded more than 35 times in a calendar year and with an annual limit of 40 $\mu g/m^3$ applicable by 2005 (Air Quality Directive 1999/30/EC). In a second stage, the annual limit of PM10 is 20 $\mu g/m^3$ with a 24 h limit of 50 $\mu g/m^3$, not to be exceeded more than 7 times in a calendar year by 2010 (Air Quality Directive 1999/30/EC). According to the United States, National Ambient Air Quality Standards (NAAQS) for PM10 should not exceed 150 $\mu g/m^3$ over 24-h periods or average more than 50 $\mu g/m^3$ on an annual basis (US EPA, 1997).

One of the many interesting aspects of the PM study is based on its composition. The airborne PM can be composed of and/or supported by organic and inorganic toxic pollutants. In fact, several studies related to the health effects of air pollution have proved the

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connection between high levels of PM and health effects through respiratory and cardiac diseases (Dockery and Pope, 1994). Concerning fine PM, there are not yet limit values for PM2.5 in the European Union, although the EC has produced the II Position Paper on PM where PM2.5 monitoring is recommended and possible limit values are supplied (EC, 2003a). In the United States, however, recent national ambient air quality standards for fine particles smaller than 2.5 μm in diameter have been set at 65 $\mu g/m^3$ over 24-h periods or 15 $\mu g/m^3$ as an annual average (US EPA, 1997).

The nature of PM can be inorganic, organic, or a mixture of them being the organic compounds contribution between 10% and 40% of the mass of PM. Among the inorganic elements constituting the PM, heavy metals and other toxic elements are an important group to be considered, which arise from different environmental sources. Some of these elements, such as As, Pb, Cd, Hg, Zn, Ni, Cu, and Cr are interesting due to their toxic character while others, such as Fe, Ca, Ba, and Mn are mainly linked to the earth's crust or resuspended soil. Some elements, like As, Ni, V, Cd, and Mn are regulated through the WHO guidelines (WHO, 2000) with a maximum value of 1000 ng/m^3 for the three first elements and 5 and 150 ng/m^3 for Cd and Mn, respectively. Pb due to its respiratory, neurological, and carcinogenic effects (Agency for Toxic Substances and Disease Registry, 1997a, b) is regulated by National Ambient Air Quality Standards with a value up to 1.5 $\mu g/m^3$ (US EPA, 1997) and by the 1999/30/EC European legislation directive with an annual limit value of 500 ng/m^3 to be met in 2010 due to its accumulative character in the human body. Because of their negative impact on human health, As, Ni, and Cd are also involved in the forthcoming EU standard, with values of 6, 20, and 5 ng/m^3, respectively, after the 2000 European Commission (EC, 2003b; EC 2003/0164 COD; EC, 2000). Other elements, like Cr, are not submitted to any regulation at the moment.

In this framework, the purpose of this study is to assess for the first time the air quality of Zaragoza, regarding the PM10 and its trace elements content. The temporal variations are analyzed in order to evaluate the behavior of these metal components and their risk for human health. Enrichment factors are considered to evaluate the strength of crustal and noncrustal sources and statistical methods based on correlation coefficients and principal component analysis (PCA) are useful for determining and distinguishing the pollution sources and their contribution.

2. Materials and methods

2.1. Study area and sampling description

The study was performed in the city of Zaragoza located in the North-East of Spain, with a population of 603 367 habitants. This city is situated in a river valley and characterized by a Mediterranean-Continental weather with an annual average temperature of 15 °C and an annual average precipitation of 367 mm mainly concentrated in 67 days (with a mean relative humidity of 67%) and being a very sunny city (2824 h/year). This city, situated at 200 m above sea level and influenced by the Mediterranean Sea and the Atlantic Ocean, is also characterized by a special kind of wind called Cierzo which comes from the Moncayo Mountain, North-West direction.

The sampling was performed close to a heavy traffic motorway and several industrial areas in which paper, steel transforming, and sugar-processing industries are placed. Samples were collected every 2 weeks from July 11, 2001 to July 25, 2002, on week days. More intensive sampling (dates: 11, 12, 13, 14, and 15 March 2002, 18, 19, 20 and 21 June 2002, 22, 23, 24, and 26 July 2002) corresponding to winter, spring, and summer seasons was carried out in order to know the daily variations of pollutants during these seasons, collecting a total of 41 samples. A Graseby Andersen High-Volume sampler provided with a PM10 cutoff inlet was used to collect particulate phase in a Teflon-coated, fiber-glass filter (0.6 μm pore size; 20.5 × 25.5 cm). The sampling time was 24 h, yielding sample volumes between 1200 and 1700 m^3.

The meteorological parameters including temperature, relative humidity, rainfall, irradiation, wind direction, and speed were provided by the Experimental Station of Aula Dei belonging to the Spanish National Institute of Meteorology.

2.2. Analysis of metals

Filters were digested twice with 10 mL of concentrated HNO_3 in a Teflon bomb to solubilize the metals in ionic form, heating almost to dryness and rinsing with HNO_3 1 N up to a final volume of 50 mL with the aim of analyzing their content in Al, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V, and Zn by ICP-OES (JY 2000 Ultrace Horiba). It is worth noting that this method does not dissolve aluminum silicate minerals and the levels for Al, Ba, K, Fe, Cr, and other naturally related elements associated to Al–Si minerals may be underestimated since HF was not used in the dissolution procedure.

Each compound was quantified under specific wavelength conditions with the corresponding dilutions using Milli-Q water, in order to be into the quantification range of each compound, and using standards which were simultaneously analyzed with experimental samples. The instrument deviation was checked at the beginning and at the end of each measured trace element. Blanks were also analyzed with trace element concentrations in all blanks less than 5% of