Geochemistry of Atmospheric Aerosols at Regional Level in the Western Mediterranean Basin

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INTRODUCCIÓN.

It is widely recognized that the Mediterranean Basin represents a unique area in terms of suspended particulate matter (Lelieveld et al., 2002; Ichoku et al., 2002). Delimited to the north by the European continent and to the south by the North African arid regions, it is largely affected by Saharan dust, marine aerosols, and anthropogenic emissions from both the highly industrialized/urbanized coastline around the Basin and the European continent. Thus the large variety of aerosol sources coupled with complex orography and atmospheric dynamics gives rise to a complex mixture of atmospheric particulate matter (PM). As a consequence of these complex scenarios the levels of fine PM (PM_1: particles with aerodynamic diameter smaller than 1μm) at regional level in the WMB recurrently are similar or even higher than those simultaneously observed at urban level. Thus, under specific winter and summer atmospheric scenarios the WMB undergoes severe pollution episodes affecting not only the coastal sites closest to the emission sources, but also the more elevated rural and remote areas land inwards due to thermally driven winds (Pérez et al., 2008; Pey et al., 2010). The origin of high fine PM concentrations at Regional Background (RB) sites in the WMB can be attributed to both the direct transport of pollutants from the coast and valleys (driven by the sea breeze) and to the transformation of secondary aerosol which take place during this transport.
Consequently, an integrated approach to aerosol observation is necessary, aimed at gaining a comprehensive understanding of aerosol properties and processes in a so complex area. This approach should include measurements of PM levels, chemical analysis and meteorological data over a large period for an improved knowledge of the mechanisms linking the local and meso-to-synoptic-scale atmospheric circulation regimes and the pollutant emissions around the WMB.

In this work we present multi-year measurements of atmospheric PM concentrations and chemical composition performed at a RB site in the WMB. Particular attention will be paid to the identification of the different winter and summer synoptic scenarios regulating the geochemistry of PM at regional level.

MEASUREMENT SITE.

Sampling of PM levels and chemical composition were performed during the period 2002 - 2010 at Montseny (MSY, 41°46'45.63"N 02°21'28.92"E, 720 m a.s.l.; Figure 1) a rural site in NE of Spain. The MSY site is part of the EUSAAR network (European Supersites for Atmospheric Aerosol Research, www.eusaar.net) recently created to integrate the measurements of atmospheric aerosol properties at 21 European ground-based stations.

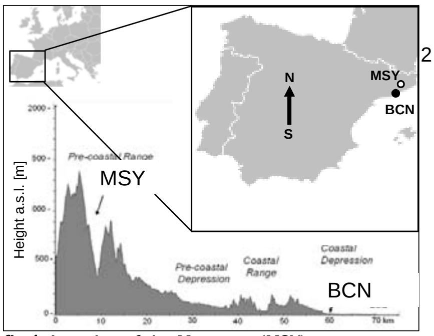

fig 1. Location of the Montseny (MSY) measurement station (720 m a.s.l.) at 50 km NNE of the city of Barcelona (BCN).

The MSY station is located within a regional natural park about 50 km to the NNE of the city of Barcelona (BCN) and 25 km from the Mediterranean coast. The selected site represents the typical regional background conditions of the WMB characterized by severe pollution episodes.

MEASUREMENTS.

PMx loadings (PM10, PM2.5 and PM1) on a 1h basis were measured by using real time optical counters (GRIMM) and PMx gravimetric measurements (24h) with high volume samplers (30 m3/h) and appropriate cut-off inlets. PMx samples collected on quartz fibre filters were analysed following the experimental procedures described in Querol et al. (2001) for the concentrations of major (Al, Ca, K, Mg, Fe, Ti, Mn, P, S, Na) and 46 trace elements and NO_3^-, SO_4^{2-}, NH_4^+ and Cl^- concentrations. Levels of OC and EC were determined from the collected filters by means of a SUNSET analyzer. Black carbon (BC) mass concentrations and particle number concentrations were measured with Multi Angle Absorption Photometers (MAAP; model 5012, Thermo), and a Condensation Particle Counters (CPC) respectively. Wind speed and direction, temperature, relative humidity, precipitation and solar radiation were also measured. Real-time measurements of concentrations of O3, CO, NO, NO2 and SO2 were provided by conventional gas phase air pollution monitors.

RESULTS.

In order to interpret the variability of PM as a function of the main different air mass transports, different meteorological tools and aerosol maps were analyzed: back-trajectories of air masses (HYSPLIT4, Draxler and Rolph, 2003); geo-potential height maps (NOAA/ESRL Physical Sciences Division, Boulder Colorado from their Web site at http:// www.cdc.noaa.gov/); and aerosol

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dust concentration maps (BSC/DREAM, NAAPS, and SKIRON). These tools allowed for the determination of the four main atmospheric scenarios usually observed in the WMB and affecting the MSY measurement site. Following the definition given in Pey et al. (2010) these were: a) Atlantic Advection (AA) episodes with air masses coming from the Atlantic Ocean; b) Winter anticyclonic episodes (WAE) causing the stagnation of air masses around the WMB for a few days and subsequent accumulation of pollutants; c) Saharan dust intrusions (NAF); and d) Regional episodes (REG) mainly recorded in summer and characterized by frequent recirculation of air masses over the WMB (Rodríguez et al., 2003; Pérez et al., 2004).

WAE episodes:
The highest levels of PMx at MSY (reaching mean values of about 30 $\mu g PM_{10}/m^3$, 23 $\mu g PM_{2.5}/m^3$ and 20 $\mu g PM_1/m^3$) were measured during the WAE episode when the air masses reside over the area under study for a few days. Under this scenario anthropogenic pollution is accumulated over the WMB and then transported to the MSY station by the sea breeze. This transport of pollutants toward the MSY under WAE scenario is constrained by the height of the Planetary Boundary Layer (PBL). The WAE episodes can be characterized by strong inversions leading to very high levels of pollution at coastal level, while inland regional sites at higher altitudes are relatively clean. Then, when the PBL height increases the accumulated pollutants are transported inland by the sea breeze thus leading to the high PM concentrations observed at RB sites. A closer analysis to the chemical PM speciated data revealed that the high levels of nitrates (NO_3^-) were the main responsible for the observed increase of fine PM levels at MSY station. Under WAE episode levels of organic matter (OM; 5-7 $\mu g/m^3$), sulfate (SO_4^{2-}; 2-3 $\mu g/m^3$), ammonium (NH_4^+; 2-3 $\mu g/m^3$) and nitrate (3-5 $\mu g/m^3$) at MSY were similar, or even higher as in the case of NO_3^-, than the levels simultaneously measured at Barcelona. As shown in this work, the high variability in PM_1 levels observed during the WAE episodes were related with the degree of recirculation of air masses over the area under study before arriving on the measurement site: The higher the number of days of recirculation, the higher the concentration of PM measured at regional level. Under WAE episode the levels of metals related with anthropogenic activities such as Cu and Sb from traffic, Zn, As, Pb from metallurgy, etc strongly rise above the usual mean levels measured at RB stations.

AA episode:
The stagnation of polluted air masses persists over the WMB and the pollutants emitted by the emission sources accumulate more and more until an Atlantic Advection episode occurs. In winter the Azores Height is frequently situated at lower latitudes giving rise to the flow of Atlantic low pressure systems into the Mediterranean (Lopez-Bustin et al., 2008). This advection of clean Atlantic air masses during the cold season causes the renovation of the previously accumulated pollution in the aged air masses. It was experimentally observed a remarkable reduction of the levels of PMx and all chemical components under AA.

REG episode:
The complex layout of the coast in the WMB, with its coastal and pre-coastal mountain ranges favours the development of small scale thermally driven flows which originate from the upslope winds driven by the sea breeze in the morning and which return back to the sea in the evening causing the formation of polluted layers with strong levels of subsidence over the coastal areas and the sea. As a consequence of the higher solar heating of the Earth's surface this phenomenon is more intense in summer when pollutants are injected into the middle troposphere up to 3.5-5 km giving rise to big convective cells involving all the WMB. Under these conditions the levels of PMx at MSY are slightly lower than under WAE episode but still considerably high (around 15 $\mu g PM_1/m^3$) given the high PBLs in summer reaching the MSY level. Conversely, at coastal areas the levels of fine PM (PM_1) are almost doubled under WAE compared with the REG episode. Concerning the fine PM mode the main responsible for the high PM1 levels under REG are OM (3-4 $\mu g/m^3$) and sulfates (2 $\mu g/m^3$).

NAF episode:
The regional background sites, located in rural environments away from the direct impact of anthropogenic sources, generally present relatively low PM_{10} and $PM_{2.5}$ levels, while, as previously observed, the levels of PM_1 may be especially high depending on the different atmospheric pollution scenarios. However, high PM_{10} can be also recorded in regional background sites, especially in southern Europe, due to the influence of African dust outbreaks which raise the levels of crustal material up to 6-9 $\mu g PM_{10}/m^3$.

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