DELIVERABLE B1.2:

4 Historical chemical composition databases

Coordinated by:

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AIRUSE

Testing and development of air quality mitigation measures in Southern Europe

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1.   SUMMARY

Source apportionment of ambient PM has been carried out at many urban areas (Portugal, Spain, Italy and Greece). Different receptor modelling approaches were employed for this purpose, based on the ambient concentration levels of particles and their chemical speciation.

The historical PM chemical composition databases were compiled at each city by AIRUSE beneficiaries and gathered in an excel file. More specifically:

- in Barcelona PM10 and PM2.5 chemical speciation data from 2007 to 2010.
- in Florence PM10 and PM2.5 chemical speciation data from September 2009 to 2010.
- in Oporto PM2.5-10 and PM2.5 chemical speciation data in 2003.
- in Athens PM10 and PM2.5 chemical speciation data from 2002 to 2003.

Due to the nature of the database it's not possible to print it, but the corresponding excel file can be found at the digital versión of this document.

2.   METHODOLOGY

From January 2013 the beneficiaries IDAEA-CSIC, UNIFI, NCSRD and UAVR conducted a literature search on previous studies, concerning emission sources conducted in urban areas in Spain, Portugal, Italy and Greece. The scientific manager A. Karanasiou compiled all the gathered information and prepared a literature review.

Additionally partners IDAEA-CSIC, UNIFI, NCSRD and UAVR gathered historical chemical composition data from the cities of Oporto, Athens, Florence, and Barcelona. The historical chemical composition databases were introduced by the scientific manager A. Karanasiou in an excel file given in this deliverable.

Furthermore, X. Querol leaded a study to interpret major 2001-2012 trends on air quality across the urban areas with a population larger than 240.000 inhabitants, as well as on 2002-2012 time series of chemical PM2.5 components from a specific site from Barcelona. The results were presented to the Spanish Ministry of Environment (MAGRAMA) and published in a scientific journal (Science of the Total Environment) with the co-authorship of MAGRAMA-AIRUSE-LIFE+: Querol X., Alastuey A., Pandolfi M., Reche C., Pérez N., Minguillón M.C., Moreno T., Viana M., et al., 2001-2012 trends on air quality in Spain. Science of the Total Environment, 490, 15 (2014), 957-969 (see Action D4 and Deliverable 12: Publications in journals and conferences).

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3.   RESULTS

Some of the results extracted from the historical chemical composition databases and the study of the time trends of air quality, are summarized below.

- **Barcelona, Spain**: The historical data from Barcelona cover the period 2003-2010. PM samples were collected from an urban background site called Palau Reial. The instrumentation used was high volume samplers (MCV, and DIGITEL) with a flow rate of 30m3/h equipped with PM10 and PM2.5 inlets. Approximately 2-3 samples (24h duration) were collected every week using quartz filters. PM10 and PM2.5 concentrations were determined gravimetrically. Subsequently, the collected filters were analyzed for water-soluble ions (NH4+, Cl-, SO42-, NO3-) by ion chromatography, major elements (Al, Ca, K, Mg, Fe, Na) by inductively coupled plasma atomic emission, ICP-AES and 46 trace elements by inductively coupled plasma mass spectrometry, ICP-MS. Organic and elemental carbon (OC and EC, respectively) was determined by a thermal–optical transmission technique using the Sunset Laboratory OCEC Analyser.

- **Oporto, Portugal**: PM samples were collected at one roadsite called Boavista, directly impacted by traffic emissions. The roadside station is part of the regional air pollution monitoring network. Two intensive, one month-long, campaigns were conducted, the first from July 3rd to July 30th and the second from November 21st to December 18th 2003. Fine (PM2.5) and coarse (PM2.5–10) fractions were collected with a Dichotomous Stacked Filter Unit, DSFU operating at 0.36 m^3/h equipped with polycarbonate membrane filters. PM2.5 and PM2.5-10 mass concentrations were determined by gravimetry. Two daily, 12 hours, sampling periods were used (starting at 7:00 a.m. or 7:00 p.m.). Sampled Nuclepore filters were analyzed regarding their inorganic chemical composition. 20 elements (Cl, Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Zr, Sn, Pb) were determined by PIXE. The water-soluble ions (Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, SO$_4^{2-}$ and NO$_3^-$) were determined by ion chromatography.

- **Florence, Italy**: The historical data from Florence cover the period March 2009 - March 2010. PM samples were collected from an urban background site called Firenze Bassi. PM2.5 was collected on a daily basis (from midnight to midnight) every even day, simultaneously on Teflon and quartz fiber filters, using a low volume sampler (FAI Hydra Dual sampler, 2.3m3/h) equipped with two PM2.5 inlets. PM2.5 concentrations were determined gravimetrically. Subsequently, Teflon filters were analyzed for water-soluble ions (Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, NO^{2-}, NO$_3^-$, SO$_4^{2-}$, Oxalate, Acetate, Glicolate, Formiate and MSA) by ion chromatography (IC), elements by Particle Induced X-ray Emission (PIXE) and selected metals by inductively coupled plasma atomic emission (ICP- AES). Organic and elemental carbon (OC and EC, respectively) were determined on quartz fiber filters by a thermal–optical transmission technique using the Sunset Laboratory OCEC Analyser

- Athens, Greece: The historical data from Athens cover the period March - December 2002. 24-hr PM2.5 samples were collected at two sites located in the Athens urban area. Both sites lie within the densely populated residential areas at the periphery of Athens city centre. PM2.5 fraction was sampled by a custom made sampling head operating at 1.38m3/h on Teflon filters (47mm in diameter). A total of 55 samples were collected.

PM2.5 mass concentrations were determined by the gravimetric method. Subsequently, part of the filters were analysed for Cd, Pb, V, Ni, Mn, Cr, Cu, Fe and Al by electrothermal atomic absorption spectrometry and for Ca, Mg, K and Na by flame atomic absorption spectrometry, AAS. The remaining parts were analysed for SO_4^{2-} by ion chromatography. In addition, black carbon concentrations (BC) were concurrently measured by aethalometer (AE-9, Maggee Sci).

Mass concentrations in these historical chemical composition databases were in general agreement with other aerosol studies at Southern Europe (Querol et al., 2009) and in the same range of levels reported for other European urban environments (Putaud et al., 2010). Sulphate and ammonium were mostly found in the fine fraction, whereas nitrate was prevalent in the coarse fraction. Carbonaceous aerosol had significant contributions in the fine fraction, revealing the strong influence of vehicle emissions. Sea-salt was the major component of coarse particles. Main sea salt components (Na^+ and Cl^-) showed higher coarse concentrations in winter, due to higher production of sea spray in wintery weather. Chloride levels decreased more strongly in summer than Na^+ as result of volatilization and substitution by acidic ions (sulphate and nitrate) on warmer sunnier days. Furthermore the equivalent ratio Cl/Na was significantly lower than the corresponding ratio (1.8) in marine aerosol indicating chloride depletion in southern Europe aerosol.

Significant correlations were observed between Al, Si, Ca, K, Mg with also the frequent association to Fe representative elements of the mineral source. High peaks of Al, Si and Ca were coincident with long-range mineral transport from northern Africa. Strong associations were found between Cu, Pb, Zn and Mn indicating the strong influence of road traffic (especially road dust resuspension) and probably industrial activities related with refuse incineration or metallurgy. Another group of species associated SO_4^{2-} and NH_4^+, having also in some cases important correlations with V and Ni, principally in the fine aerosol fraction. These species represent secondary aerosol particles resultant from the oxidation of SO2, emitted from fuel oil combustion (association with V and Ni), giving rise to the nucleation and condensation of sulphuric acid, totally or partially neutralized by ammonia.

The historical chemical composition datasets will be compared with the new datasets created after the finalization of Action B2, in order to detect any increasing or decreasing trend of elemental compositions in the region of southern Europe.

4.   RFERENCES

PUTAUD J-P., et al. (2010). European Aerosol Phenomenology - : physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. Atmospheric Environment Atmospheric Environment 44 (2010) 1308-1320.

QUEROL X., et al. (2009). Variability in regional background aerosols within the Mediterranean. Atmospheric Chemistry and Physics. 9, 4575-4591.

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