FINAL REPORT

DELIVERABLE B3.1:

Souther European database for concentrations of chemical tracers for natural sources

Coordinated by:

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LIFE11 /ENV/ES/584

AIRUSE

Testing and development of air quality mitigation measures in Southern Europe

Index

1. SUMMARY

The contribution of natural sources in particulate matter (PM) concentrations has been assessed for 5 Southern European cities: Porto (Portugal), Barcelona (Spain), Milan and Florence (Italy) and Athens (Greece). LIFE-AIRUSE project has focused on two major natural sources: long-range transport of African dust and sea salt. Contribution from wildfires has been also detected in one city, Porto, during the studied period.

A database on the impact of natural source has been compiled, including concentrations of PM and chemical tracers used for the identification and quantification of African dust and sea salt contributions, as well as the calculated African net dust, and sea salt concentrations for each city. In addition, wildfires' contribution is provided for Porto. Both PM_{10} and $PM_{2.5}$ concentrations are reported for a total of six sites:

- Porto urban traffic site, POR-TR
- Barcelona urban background site, BCN-UB
- Milano urban background site, MLN-UB
- Florence urban background site, FI-UB
- Athens suburban site, ATH-SUB
- Athens urban traffic site, ATH-TR.

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 version of this document.

2. METHODOLOGY

2.1. Chemical tracers

Chemical tracers for natural sources include: Na and Cl (for sea salt), Al, Si and Ti (for the determination of the PM mineral component) and Al, Si and CO_3^{2-} as tracers of African dust transport. Concentration data on the relevant PM_{10} and $PM_{2.5}$ chemical components were obtained through year-long measurement campaigns conducted at each city. The measurement period, type of monitoring site and number of valid chemical speciation samples are presented in Table 1. The analytical methods used for chemical speciation are provided in Table 2.

Table 1 - Description of measurement campaigns.

Monitoring site	Measurement period	Number of valid samples
Porto – Urban traffic site (POR-TR)	01/2013 -01/2014	122 (PM_{10}) / 125 ($PM_{2.5}$)
Barcelona – Urban background site (BCN-UB)	01/2013 -01/2014	125 (PM_{10}) / 109 ($PM_{2.5}$)
Milan - Urban background site (MLN-UB)	01/2013 - 01/2014	276 (PM_{10}) / 357 ($PM_{2.5}$)
Florence – Urban background site FI-UB)	01/2013 - 01/2014	223 (PM_{10}) / 243 ($PM_{2.5}$)
Athens – Suburban site (ATH-SUB)	02/2013 - 02/2014	192 (PM_{10}) / 212 ($PM_{2.5}$)
Athens – Traffic site (ATH-TR)	07-08/2013 & 01-02/2014	57 (PM_{10}) / 53 ($PM_{2.5}$)

Table 2 – Chemical characterization methods employed at each city.

Porto		**Barcelona**		**Milan**		**Florence**		**Athens**	
Na^+ Cl^-	IC	Cl-	IC	Na^+ Cl^-	IC	Na^+ Cl^-	IC	Na^+ Cl^-	IC
Al, Si Ti	PIXE	Na Al	ICP-AES	Al Si Ti	XRF	Al Si Ti	PIXE	Al Si Ti	PIXE
		Ti	ICP-MS						
CO_3^{2-}	IR	CO_3^{2-}	IR	CO_3^{2-}	IR	CO_3^{2-}	IR	CO_3^{2-}	IR

IC: Ion chromatography; PIXE: Particle-Induced X-ray Emission; ICP-AES: Inductively Coupled Plasma Atomic Emission Spectroscopy; ICP-MS: Inductively Coupled Plasma Mass Spectroscopy; IR: Acidification / Infrared CO_2 analyser (Pio et al., 1994).

2.2. African dust

Potential African dust transport events at each city were identified through the application of the following modelling tools:

- The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) Model (Draxler & Rolph, 2003);
- The Barcelona Supercomputing Centre (BSC) - DREAM8b v2.0 Atmospheric Dust Forecast System;
- The Skiron forecast model of the National and Kapodistrian University of Athens;
- The Flextra model.

Following the identification of days potentially affected by long-range transport of African dust, net African dust concentrations were calculated based on the methodology proposed by EC (Escudero et al., 2007; SEC 2011.208). This method requires continuous 24-hr PM data from a background site representative of the regional background concentrations at the studied area. PM_{10} and $PM_{2.5}$ data available from the National Monitoring Networks operating at the 5 cities were used for this analysis. 30-days moving averages of the previous and next 15 days of the regional background concentrations were calculated, excluding days with potential African dust transport. Averages corresponded to 40^{th} percentiles in the case of Porto, Barcelona and Florence, according to EC guidelines (SEC 2011.208). In Milan and Athens, a more conservative indicator was selected as suggested by the guideline above, the 50^{th} percentile, since it was found to reproduce better PM_{10} background concentrations. In the case of Florence, $PM_{2.5}$ regional background data were not available. For that reason, African dust contribution was estimated based on the Saharan dust source identified by receptor modelling (Positive Matrix Factorization, PMF) at this site.

The PM mineral component was used in sensitivity analysis on the quantification of African net dust concentrations. The formula used for its calculation was based on Al, Si and Ti concentrations (Malm et al., 1994):

$$\text{Minerals} = 1.15*(3.79*Al+2.14*Si+1.67*Ti) \quad (1)$$

2.3. Sea salt

Contribution of sea salt was calculated from major sea salt components (Cl and Na) and typical elemental ratios for sea water (Mg/Na, K/Na, Ca/Na and SO_4^{2-}/Na) and earth's crust (Na/Al):

$$\text{Sea salt} = Cl + ssNa + ssMg + ssK + ssCa + ssSO_4^{-2} \quad (2)$$

where: ss: sea salt, nss: non-sea salt and

$$ssNa = Na – nssNa \quad (3)$$

$$nssNa = 0.348*Al \quad (4)$$

$$ssMg = 0.119*ssNa \quad (5)$$

$$ssK = 0.037*ssNa \quad (6)$$

$$ssCa = 0.038*ssNa \quad (7)$$

$$ssSO_4^{2-} = 0.253*ssNa \quad (8)$$

2.4. Wildfires

Uncontrolled forest fires were not among the natural sources to be examined by LIFE-AIRUSE project. Nevertheless, several wildfires were registered in the Porto district during late August and September of 2013, a particularly hot and dry period. According to the Institute for Nature Conservation and Forests (ICNF, 2014), this district recorded the highest number of occurrences and one of the largest burnt areas. These events were also identified by receptor modelling. The biomass burning source found in Porto by PMF presented several peak concentrations during this period. These concentrations were therefore attributed to wildfires and classified as natural source contributions.

3. RESULTS

A summary of the results on the contribution of natural sources to PM_{10} and $PM_{2.5}$ concentrations at the AIRUSE cities is provided below.

African dust contribution to PM concentrations was more pronounced in Eastern Mediterranean (Athens), with peak concentrations during spring time, reaching up to a 24-hr concentration of 127 μg m^{-3} during a 15-day dust transport event on May 2013. The mean annual relative contributions of African dust to PM_{10} concentrations decreased from East to West: 21% in Athens, 5% in Florence, and around 2% in Milan, Barcelona and Porto. The respective contributions to $PM_{2.5}$ concentrations were 13.7% in Athens, 1.3-1.4% in Florence and Milan and 2.3-2.4% in Barcelona and Porto. African dust inputs were highest during spring and lowest during summer in Athens and Florence. Milan presented high contributions during spring and summer, Porto during winter and Barcelona during summer season.

Sea salt was mostly related to the coarse mode and exhibited significant seasonal variability. Sea salt concentrations were highest in Porto, with average relative contributions equal to 12.3% and 4.6% for PM_{10} and $PM_{2.5}$. The respective contributions for Athens and Barcelona were 7–8% to PM_{10} and 2.3-2.5% to $PM_{2.5}$. The lowest contributions were observed in Florence and Milan (1.3-3.3% to PM_{10}). The results reflect the geographical distribution of AIRUSE sites: lower levels of sea salt at the inland Italian cities (Florence and Milan) and higher at the Mediterranean coastal sites, with the highest contribution observed at the Atlantic site (Porto). The comparison of the two sites in the Greater Athens Area (ATH-SUB and ATH-TR) revealed significant spatial variability in sea salt concentrations.

Uncontrolled forest fires were observed to affect PM concentrations only in Porto during the studied period. The average contribution to PM levels was low (1.4% and 1.9% to PM_{10} and $PM_{2.5}$, respectively) due to the few event days during the year (after the 20th of August and during September). Nevertheless during event days contribution to PM was greatly increased, reaching 20 and 22% to PM_{10} and $PM_{2.5}$, respectively.

The subtraction of natural sources' contribution from PM_{10} concentrations measured at the AIRUSE sites, according to EC regulation, led to a decrease in mean annual PM_{10} concentrations in the range of 3.5 (Milan) – 29.5% (Athens). Attainment of the annual limit value set by EU through Directive 2008/50/EC was achieved at all sites during 2013, although the urban background site in Milan and the urban traffic site in Porto exhibited concentrations close to the air quality standard. Similar decrease (1.5 – 21%) was observed in the 90.4th percentiles of PM_{10} concentrations. The 90.4th percentile corresponds to the maximum permissible number of exceedance days (35 during the year). The subtraction of natural sources' contributions led to marginal compliance with the 24-hr limit value for Porto, while Milan continued to present more exceedances than the permitted 35 days (84 days for PM_{10} and 82 days for the adjusted PM_{10} after subtraction of natural sources' contribution).

The Potential Source Contribution Function (PSCF) model was implemented in order to locate natural contribution source regions. PSCF has been successfully applied in several cases of long-range transport of aerosol species from distant sources (Polissar et al., 2001; Eleftheriadis et al., 2009). This advacnced tool was used to confirm in an independent way that the natural source contributions from distant sources were determined with higher confidence, by linking the relevant natural components with their geographical source areas. PSCF analysis revealed the specific source areas in Africa connected to the long-range transport of desert dust to Southern European countries. In addition, the analysis clearly indicated as the source of peak CO_3, Al and Si concentrations two well known regions in Eastern and Western Sahara (Spyrou et al., 2010), validating the use of these species as tracers for African dust transport. PSCF results on sea salt demonstrated that the highest peaks of sea salt contributions appear to be related with long range transport of oceanic air masses. Local meteorology thus may be inappropriate as an indicator of these contributions while concentrations of Na can be a more valuable tracer for quantification.

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