COMBINING DIFFERENT METHODOLOGIES FOR SOURCE APPORTIONMENT OF PARTICULATE MATTER IN CYPRUS

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Abstract: For Mediterranean countries like Cyprus, controlling particulate matter (PM) exceedances of the EU limit values with the enforcement of national air quality plans is a major challenge, due to the contribution of transboundary and natural emission sources. Cyprus is particularly affected by sea-salt aerosols and dust from the Saharan and the Middle East deserts. According to the 2008/50/EC Directive on ambient air quality and cleaner air for Europe, exceedances that can demonstrably be attributed to natural sources can be excluded from the assessment for the purpose of the Directive. In order to justify such exception claims, Member States have to provide quantitative evidence for demonstrating the contribution of natural emissions to national, urban and local particle concentrations. In response to this need, considerable progress has been made in regard to PM source apportionment in Cyprus by following an integrated approach using different methodologies. On the basis of measured data from regional background, residential background and urban traffic stations, an interpretation of the exceedances registered in each station was carried out by analysing meteorological information, available satellite data and modelling simulations. In order to identify the different source regions of the air masses reaching the study area, 5-day back trajectories at different altitudes were calculated for each exceedance day, using a Lagrangian trajectory model. The influence of African dust transport was investigated by means of aerosol maps and satellite imagery, while the source apportionment study was complemented by the application of the EPA PMF 3.0 receptor model in four urban traffic sites and one regional background station in Cyprus.

Key words: *source apportionment, particulate matter, natural sources, air quality policy.*

INTRODUCTION

The present paper summarises the several approaches used to perform source apportionment of particulate matter in Cyprus, in a study focusing on the contribution of natural sources on ambient concentrations of PM_{10}. This study initially aimed to support Cyprus national authorities in preparing the application of Cyprus for a postponement regarding the attainment of PM_{10} limit values, on the basis of substantial contribution of natural sources. According to the 2008/50/EC Directive on ambient air quality and cleaner air for Europe, exceedances that can demonstrably be attributed to natural sources can be excluded from the assessment for the purpose of the directive. In order to justify such exception claims, Member States have to provide quantitative evidence for demonstrating the contribution of natural emissions to national, urban and local particle concentrations. In response to this need, accurate and reliable source apportionment is of imperative importance. The study considered the official European Commission guidelines on the estimation of the contribution of natural sources to PM_{10} concentrations (Guidance on the quantification of the contribution of natural sources under the EU Air Quality Directive 2008/50/EC). The source apportionment analysis was at a later stage extended to provide quantitative information on the main polluting sources in Cyprus regarding $PM_{2.5}$, and also to include specific PM sources that were considered important (such as mining activity).

This work follows closely the activities of Sub-Group 2 on the "Contribution of natural sources and source apportionment" of FAIRMODE (Forum for Air Quality Modelling in Europe, URL1), while the source apportionment methodology used in Cyprus is an attempt towards promoting harmonised model use for source apportionment in the EU.

Study objectives

Taking into consideration the contribution of natural particle emission sources to the air pollution in Cyprus, the source apportionment study initially focused on supporting the application of Cyprus for a postponement of three years after the entry into force of the directive regarding the attainment of PM_{10} limit values (URL2). For this purpose, observational data and model results for the year 2007 were

examined in order to quantify the dust levels in Cyprus due to natural sources and demonstrate its contribution to exceedances of the limit values. To facilitate the synthesis of the data, all exceedance situations for 2007 aerosol episodes were identified and analysed. The study was complemented with source apportionment analysis using receptor modelling based on surface observation data and chemical analysis data for the year 2008. More specifically, that study aimed to:

1) Collect, analyse and present PM_{10} concentration levels at the regional, urban and local scales for the years 2007 and 2008 in Cyprus. Concentrations are reported using relevant statistical indices, maps, diagrams and figures.
2) Identify the main natural emission sources of primary particles in Cyprus and classify the main exceedance situation categories
3) Apply appropriate source apportionment analysis, based on EU guidelines for policy related air quality assessment, to quantify the relevant contributions at the regional, urban and local scales for years 2007 and 2008.

METHODOLOGY

For the purposes of this study, data from air quality stations operated by the Department of Labour Inspection of the Ministry of Labour and Social Insurance were analysed. Data for years 2007 and 2008 were compiled from the nine stations of the national monitoring network but a large part of the analysis concentrated on three stations that were considered representative: the regional background station at Agia Marina (Xyliatou) which belongs to the EMEP network and is located at a rural area away from major anthropogenic sources, a residential background station operating in a residential area in the city of Larnaca (in some cases also the residential station of Nicosia was considered) and an urban traffic station located in downtown Nicosia. An extensive sampling campaign was undertaken in 2008, resulting to a large number of chemical analysis data.

The following methods were combined for source apportionment analysis:

1. Air quality assessment data from different stations were examined along with meteorological data (synoptic conditions, wind speed and direction, rainfall) to classify exceedance situations and identify the conditions leading to air pollution episodes in Cyprus.
2. The combined analysis of back trajectories, aerosol model results, aerosol maps and satellite images was used for the classification of exceedance situations in Cyprus.
3. The subtraction of the 30^{th} percentile method and of the sea salt ion ratios were the methods used to quantify long range dust and sea salt PM_{10} contributions for the year 2008, according to the Guidance on the quantification of the contribution of natural sources under the EU Air Quality Directive 2008/50/EC.
4. Receptor modelling (Enrichment Factor analysis and Positive Matrix Factorisation) was applied using 2008 data.

RESULTS

The main findings of the PM_{10} source apportionment analysis using the different methodologies are presented in the following sections.

Analysis based on measured concentration values at different stations

An assessment of the air quality status in the air quality zone of Cyprus for 2007 was initially undertaken, using observation data from nine stations of the national monitoring network, operated by the Department of Labour Inspection of Cyprus. The stations represent air quality at different spatial scales, namely the regional (Agia Marina), urban (Larnaca Residential) and local (Nicosia Hospital, Larnaca Traffic, Limassol Traffic, Pafos Traffic, Zygi Industrial) scales. Annual average PM_{10} concentrations measured at different stations for 2007 indicated that concentration values were higher at the traffic stations due to increased emissions from traffic or industry, although PM_{10} observations in the urban background station in Larnaca were almost at the same level with the rest of the local stations. At all stations except for Agia Marina, PM_{10} values exceeded the annual EU limit of 40 $\mu g/m^3$. In terms of the PM_{10} daily limit value, a significantly higher number of exceedances were recorded at the traffic stations, as expected. However, the exceedances observed at the station of Agia Marina are marginally at the level of 35 exceedances per year, as specified in the EU Air Quality Directive. Taking into consideration the limited contribution of

anthropogenic sources to the PM_{10} concentration values measured at Agia Marina, the relatively high maximum concentration value of 469.2 μg/m^3 was a first important indication for the importance of natural emission sources and dust transport. It is also interesting to notice the seasonal variability of PM_{10} concentration values at the different stations (Figure 1). A number of simultaneously occurring peaks in the time series of all stations may be used as an indication of transboundary pollutant transport, for example from the Saharan desert. Meteorological conditions (wind speed and direction) and topographical features at each station were also correlated with concentrations. In the case of Agia Marina, high PM_{10} levels were associated with relatively low winds of south-easterly direction, indicating dust flow from both North Africa and the Middle East.

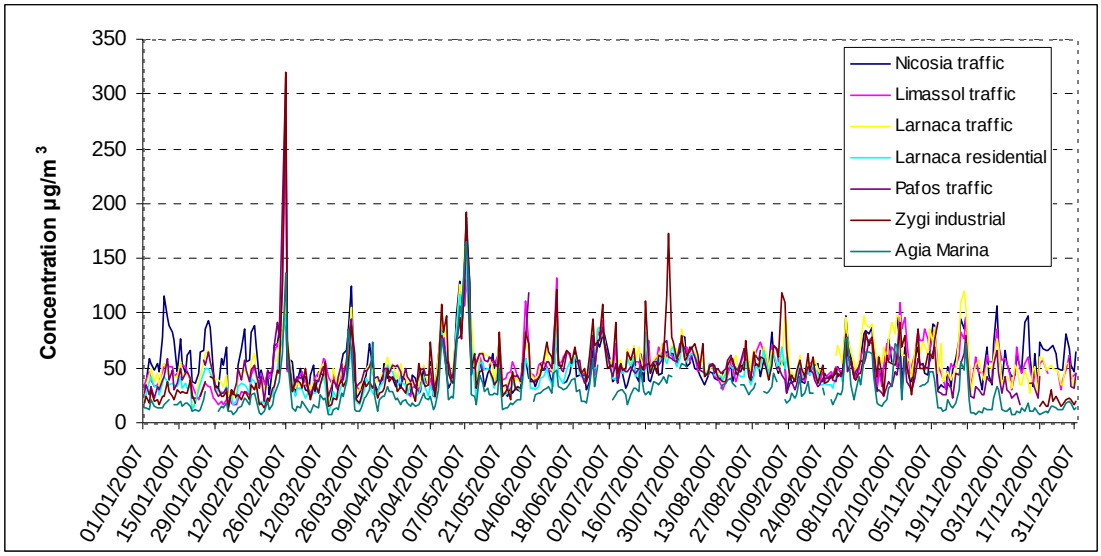

Figure 1 Seasonal variability of PM_{10} concentration values at different stations in Cyprus for the year 2007.

Classification of exceedance situations

Following the assessment of air quality for 2007, identification and classification of exceedance situations was performed. Exceedances of measured PM_{10} daily concentrations in the main three station locations (Agia Marina, Larnaca residential and Nicosia traffic) were classified according to their major emission source attribution, using a combination of back-trajectory modelling, study of synoptic maps and assessment of dust transport in the Eastern Mediterranean region. In order to interpret the different source regions of the air masses reaching the study area, 5-day back trajectories at different altitudes (500, 1500 and 2500m a.s.l.) for each day with exceedance of the limit value, were calculated with the HYSPLIT4 model (Draxler, R.R. and G.D. Rolph, 2003). The influence of African dust transport was investigated by means of the NAAPs aerosol maps provided by the Naval Research Laboratory and satellite imagery supplied by MODIS. Finally, dust load and sea salt surface concentrations calculated with the DREAM-8b model of the Tel Aviv University (Nickovic, S. et al, 2001) were used.

Four different types of major emission contributions were identified, leading to a corresponding classification of episodes into four distinct classes (Figure 2):

a) “Saharan”, which includes situations of advective transport from the Sahara and Sahel desert regions and were identified primarily from 5-day back-trajectory calculations as well as the presence of persistent anticyclonic conditions in the region.

b) “Middle Eastern”, which consists of episodes of dust transport primarily from areas of the middle-east (Saudi Arabia, Jordan, Syria, Iraq), is yet again identified from back-trajectories as well as from regional-scale dust concentration maps calculated by the NAAPS model.

c) “European”, which includes advective contributions from northern Balkan countries and from areas in central and northern Europe. Those kinds of episodes are usually associated with advective transport of polluted air masses due to anthropogenic activity in mainland Europe. This of course can be either primary emitted PM or secondary particles formed in the atmosphere.

d) “Non-advective”, which covers the remaining episodes which represent meteorological cases of weak synoptic forcing combined with low persistent background concentrations of PM_{10}.

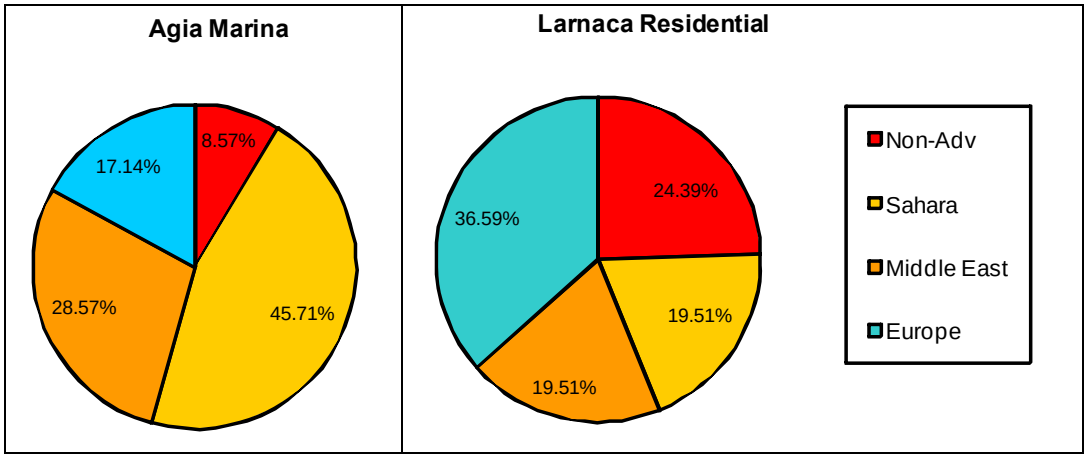

Figure 2. Classification of PM_{10} exceedance situations in a regional background station and a residential station in Cyprus.

It was found that Saharan dust situations are the prevailing type of event (45.71%) in the regional background station (Agia Marina), with non-advective episodes being the rarest type of episode (8.57%). The situation is quite different in the other two stations as non-advective episodes are much more frequent (at almost 25% of the cases at both the residential and the traffic stations). Those episodes are in many cases associated with stagnant conditions and local dispersion phenomena.

Quantification of Saharan transport and sea salt contributions

In order to extend the PM_{10} source apportionment study in Cyprus, measured concentrations and chemical analyses data from 2008 were also examined for the estimation of dust transport and sea salt contributions, respectively. Saharan dust transport contribution was calculated using the monthly moving PM_{10} 30^{th} percentile value from the data time series (excluding days with identified African influence) of the regional background station, according to the methodology proposed by Escudero, M. et al. (2007). The 30^{th} percentile value was then subtracted from the bulk PM_{10} levels recorded during the Saharan transport day at the relevant regional background station in order to obtain the daily net dust load.

Sea salt contribution to PM_{10} levels at each station for 2008 was quantified on the basis of the chloride and sodium ion concentrations, obtained after chemical analysis of collected aerosol samples. The methodology assumed that sea salt is made up entirely by NaCl and that all Na and Cl are associated in sodium chloride (Guidance on the quantification of the contribution of natural sources under the EU Air Quality Directive 2008/50/EC). The results of the source apportionment analysis for 2008 suggested that out of the 135 daily exceedances reported at the Nicosia traffic station, 72 exceedances could be attributed to natural sources (sea salt and Saharan dust), while 63 exceedances were due to local factors (such as traffic emissions).

Results from EF analysis

Enrichment Factor (EF) analysis and multivariate receptor modelling were applied for PM_{10} source identification at the regional background station of Agia Marina and the traffic and residential stations of Nicosia, according to the methodology by Bari, M.D. et al. (2009). The results obtained from the chemical analysis of the soil samples from the three stations were used for source apportionment performed by means of enrichment factors and positive matrix factorisation modelling. The results indicated that the major emission sources of PM_{10} concentrations at the three characteristic sites were local mineral soil, sea salt, road dust, oil combustion, secondary pollutants and gasoline vehicles. The resuspension factor was found to result in significant contributions at the traffic station (13.7% of measured PM_{10} values) and at the residential station (5.6% of measured PM_{10} values), but not at the regional background station. It can be demonstrated that for the dry conditions on the island, the

resuspension of local mineral soil and resuspended road dust contribute decisively to the PM_{10} load at the traffic and residential sites. Local mineral soil was found to be an important natural source of PM_{10} at the residential (9.1%) and regional background (14.2%) stations. Sea salt was found to be the largest contributor to PM_{10} considered as being of natural origin at all three stations (41% at Nicosia traffic, 44% at Nicosia residential and 50.7% at Agia Marina). Second to sea salt, traffic pollution was the largest contributor to PM_{10} levels at Nicosia traffic (28%), while secondary pollutants and oil combustion were more important sources at Nicosia residential station (26.8% and 13% respectively).

Results from PMF analysis

Following the study on the contribution of natural sources in PM_{10} levels in Cyprus for the year 2007, a receptor modelling study was undertaken to assess the impact of the main emission sources in the concentration levels of PM_{10} in Cyprus. The Positive Matrix Factorisation (PMF) method was applied for a three-year period between 2008 and 2010. The data used for the application were derived from chemical analyses conducted for samples originating from five stations of the Cypriot air quality monitoring network. The stations included the traffic stations of Nicosia, Larnaca, Limassol and Pafos, as well as the rural background station of Agia Marina. The total number of the hourly samples for the chemical analyses reached 3000 regarding the period mentioned above. The tracers used for the attribution of the factors calculated by PMF to the major emission source categories contained eleven metal ions (Fe, Cu, Al, Co, V, Ti, Mn, Sn, Zn, Ba and W) related to human activities and natural sources. The main water-soluble ions found in the usual particulate matter composition, such as NO_3 and SO_4^2, were used to mark secondary aerosols. Na, Mg and Cl ions were used in order to trace sea salt.

The application of the PMF method demonstrated four major emission categories which affect the particulate pollution levels as regards the Cypriot hot spots. For the Larnaca traffic station, the analysis of the PMF results shows that road transport has the most significant contribution to the PM_{10} concentration levels (34.6% of the mean PM_{10} value for 2008). This particular category includes the resuspension of road dust due to the motion of the vehicles in addition to the exhaust fumes. However, natural sources (sea salt and Saharan dust) are found to be almost equally responsible for exceedances, contributing to a 32.8% to PM_{10} concentrations. Finally, there is also a factor that is difficult to be attributed to a specific emission category (unidentified factor), which depicts the contribution of other human activities such as industry and central heating.

CONCLUSIONS

A source apportionment study for Cyprus using a combination of methods including, observational data analysis, receptor modelling results and consultation of aerosol model results, maps and satellite images was undertaken for the years 2007 and 2008. Quantification of the contribution of natural sources, particularly of Saharan dust transport and sea salt was performed based on the guidelines included in the Guidance on the quantification of the contribution of natural sources under the EU Air Quality Directive 2008/50/EC. The results confirm the significant contribution of natural sources to PM_{10} exceedance situations at the residential and rural sites in Cyprus and demonstrate an integrated methodology for source apportionment purposes to comply with policy requirements.

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