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Assessing the Performance of Methods to Detect and Quantify African Dust in Airborne Particulates

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African dust (AD) contributions to particulate matter (PM) levels may be reported by Member States to the European Commission during justification of exceedances of the daily limit value (DLV). However, the detection and subsequent quantification of the AD contribution to PM levels is complex, and only two measurement-based methods are available in the literature: the Spanish−Portuguese reference method (SPR), and the Tel Aviv University method (TAU). In the present study, both methods were assessed. The SPR method was more conservative in the detection of episodes (71 days identified as AD by SPR, vs 81 by TAU), as it is less affected by interferences with local dust sources. The mean annual contribution of AD was lower with the TAU method than with SPR (2.7 vs 3.5 ± 1.5 μg/m^3). The SPR and TAU AD time series were correlated with daily aluminum levels (a known tracer of AD), as well as with an AD source identified by the Positive Matrix Factorization (PMF) receptor model. Higher r^2 values were obtained with the SPR method than with TAU in both cases (r^2 = 0.72 vs 0.56, $y = 0.05x$ vs $y = 0.06x$ with aluminum levels; r^2=0.79 vs 0.43, $y = 0.8x$ vs $y = 0.4x$ with the PMF source). We conclude that the SPR method is more adequate from an EU policy perspective (justification of DLV exceedances) due to the fact that it is more conservative than the TAU method. Based on our results, the TAU method requires adaptation of the thresholds in the algorithm to refine detection of low-impact episodes and avoid misclassification of local events as AD.

Introduction

European directives on air quality take into account the potential exceedance of the particulate matter (PM) daily limit values due to the influence of natural sources, including "*the transport of natural particles from arid regions*" (article 2.15, 2008/50/EC). In these cases the exceedances caused by natural episodes may be taken into account for air quality evaluation after careful justification of their natural origin by the Member States.

To carry out this justification, the EU Environmental Office in the document "Guidance for State Members on PM_{10} Measurements and the inter-comparison with the reference method" (*1*) published a methodology that enabled Member States to identify days with African dust (AD) transport. This methodology is based on the evaluation of satellite imagery, aerosol maps, and back-trajectory analysis. However, it is only qualitative and it does not allow for the quantification of AD contributions to PM levels.

Currently, two measurement-based methodologies (non model-based) may be found in the literature to detect and quantify AD contributions to PM levels:

• Escudero et al. (2007) and Spanish Ministry of the Environment, Rural and Marine Affairs (2010) (*2, 3*): a joint methodology developed by Spain and Portugal that detects AD events by means of back-trajectories, satellite imagery, and aerosol maps (based on ref *1*). Subsequently, AD contributions are estimated using a statistical method based on the calculation of the 30 days moving 40th percentile for PM_{10} levels at regional background sites (see details below; *3*). The Spanish−Portuguese reference method (SPR method, from now on) is included as a reference method in the text "Guidance on the quantification of the contribution of natural sources under the EU Air Quality Directive 2008/50/EC", currently in draft version (*4*).

• Ganor et al. (2009) (*5*): a method developed by the Tel Aviv University to identify and quantify AD using only hourly PM_{10} and $PM_{2.5}$ measurements from automatic stations. The method does not require any other inputs such as satellite observations, model back-trajectories, dust forecast models, or mineralogical analyses. It employs an automatic algorithm with three thresholds (see details below). From now on, this method will be referred to as the TAU method.

In addition, a number of model-based approaches may also be found in the literature (*6, 7*). However, model-based quantitative approximations of AD contributions are still far from estimations produced by experimental ground-based and column measurements. In general, the main limitations of the models are related to the determination of the height at which AD is transported (the vertical dispersion of dust within the air column) and their spatial resolution (grid size). Consequently, in the present work only experimental approaches will be discussed.

The quantification of AD contributions to PM levels may be considered complex due to the specific characteristics of these aerosols:

• During AD outbreaks in Southern Europe and the Mediterranean (*8*−*13*), the physical−chemical properties of AD may vary as a function of their source regions (*15, 16*) and atmospheric transport mechanisms (*10, 17*−*19*).

• Due to the fact that AD is mainly constituted by mineral dust (in addition to secondary aerosols from interaction with local gaseous precursors, *20*), the chemical composition of AD presents marker elements similar to those of local dust in Southern Europe. The similarity between the chemical compositions of different emission sources gives rise to collinearity constraints when receptor modeling techniques are applied (see below) (*21, 22*).

Receptor models (*23*) are a widely used tool for the discrimination of aerosol sources in atmospheric sciences.

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However, mineral matter of African origin is seldom discriminated as a single independent source of PM. Conversely, it is generally grouped with other sources of mineral dust. To the authors' knowledge, to date AD was only identified by a receptor model as a single source of PM in one study (*24*), whereas it was not discriminated in source apportionment studies in other sites in Spain (*25*) (>30 study locations), Portugal (*26*), Turkey (*27*), Cyprus (*28*), or Italy (*29*). Consequently, receptor models are hereby not presented as an alternative to the experimental methods described above, but as a potential tool to compare or complement their results.

The aim of the present work is 2-fold:

(a) To assess the ability of the Spanish−Portuguese reference method (SPR) and the Tel Aviv University method (TAU) to identify and quantify AD episodes. Their results will be compared with time series of Al (known tracer of AD) and with receptor modeling results (using Positive Matrix Factorization, PMF (*24*)). Sensitivity analyses of the SPR and TAU methods will be carried out.

(b) To prove that receptor models may discriminate AD as an independent PM source, by using PMF.

Material and Methods

SPR Method. *Description of the Method.* AD episodes are detected with the SPR method at a given location by means of a combination of tools which include back-trajectory analysis (NOAA-Hysplit http://ready.arl.noaa.gov/HYSPLIT-.php), satellite imagery (NASA-SeaWIFS http://oceancolor.gsfc.nasa.gov/SeaWiFS/), and aerosol dust maps (SKIRON http://forecast.uoa.gr/, BSC-DREAM http://www.bsc.es/projects/earthscience/DREAM/, NRL-NAAPS http://www.nrlmry.navy.mil/aerosol/). Once the episodic days are identified, the goal is to discriminate AD from the local or regional-scale dust (arising from dust resuspension processes, city dust, etc.), and to quantify it. The daily regional background PM_{10} level for days without AD is calculated as the 30 days moving 40th percentile for PM_{10} levels at a regional background site (belonging or not to the EMEP network, European Monitoring and Evaluation Programme), after removal of the episodic days from the time series. Subsequently, the difference between the regional background level on days without AD, and on days with AD, is used to estimate the daily contribution of AD. This daily contribution of AD may then be subtracted from the daily PM levels at urban background locations. Prior studies (*3*) showed that the 30 days moving 40th percentile reproduces rather suitably the regional PM background under advective atmospheric conditions (not discussed in the present work). Initially, the 30th percentile was used (*3*), but it was subsequently discarded in favor of the 40th percentile (*2*).

The Present Analysis. AD contributions were calculated at the Atazar regional background site (40°56′4″ N, 3°28′19″ W, 995 m a.s.l.) located at a 65 km distance from Madrid (central Spain), between January and December 2007. The PM_{10} data were obtained by means of automatic instrumentation (Beta). In total, 362 valid daily PM_{10} means were available. The daily AD contributions obtained at the Atazar site were then subtracted from the daily PM_{10} levels at the urban site at Escuelas Aguirre (Madrid, 40°25′32″ N, 03°40′52″ W, 672 m a.s.l.) and the urban background site at Casa de Campo (Madrid, 40°25′18″ N, 03°44′56″ W, 645 m a.s.l.) to calculate the non-African contribution in Madrid.

TAU Method. *Description of the Method.* The TAU method aims to identify and quantify AD using only hourly PM_{10} measurements from automatic stations (*5*). The automatic algorithm uses three thresholds, whereby an episode is identified as an AD event only if the following apply: the half-hour PM_{10} average is above 100 $\mu g/m^3$, this level is maintained for at least 3 h, and the maximum concentration recorded is above 180 $\mu g/m^3$. To quantify AD, the TAU method calculates the difference between the average PM_{10} during a given period and the average PM_{10} without AD contributions for that same period (*5*).

The Present Analysis. No indications are provided in the Ganor et al. (*5*) paper regarding the type of monitoring station to be used for the application of the TAU method. In the present work, an urban background site (Casa de Campo) was used, given that the anthropogenic influence in PM at the Escuelas Aguirre site were considered too high, and thus the hourly PM increments due to AD were expected to be less visible than at an urban background site as Casa de Campo (this is no limitation for the SPR method). The analysis was carried out for PM_{10}, using TEOM automatic hourly data. AD contributions were calculated for the period January to December 2007 (8722 valid hourly data points).

Receptor Modeling: Positive Matrix Factorization.

Description of the Method. Receptor modeling analysis was carried out using the offline PMF2 version (*30*) provided by P. Paatero at University of Helsinki, Finland. Receptor models assess correlations between the input variables and provide as output a number of factors which are interpreted as emission sources. By means of multilinear regression analysis, the contribution of each source to the total PM mass is calculated.

The Present Analysis. Daily PM_{10} levels were obtained at the Escuelas Aguirre urban location between January and December 2007. Sampling was carried out 2 days per week on quartz fiber filters by means of one PM_{10} Andersen high-volume reference sampler (EN 12341:1998 standard, 68 m^3/h). In total, 94 valid PM_{10} samples were collected. Input data were obtained by chemical analysis of the filter samples following the methodology described elsewhere (*31*).

The PM_{10} matrix used as input included 94 cases and 36 variables. FPEAK was set to a constant value of 0.0, and results were interpreted as the raw output of the model, with no use of Gkey or Fkey functions to modulate the model's output (*24, 34, 35*). Uncertainties were calculated based on Polissar et al. (*35*) and modified to include both the measurement errors and the variability in the blank concentrations. On average, calculated errors ranged from 12% to 59% of the mass of the variables.

Results and Discussion

SPR Method. The net AD was calculated for the study period based on the 30 days moving 40th percentile (*2*), taking as reference the regional background air quality monitoring site Atazar. The time series of AD events identified is shown in Figure 1 (top), with 71 episodic days in 2007. In terms of mass, daily AD contributions ranged from 2 to 48 $\mu g/m^3$ in PM_{10} (with 1.5 $\mu g/m^3$ uncertainty (*32*)), with an annual contribution of 3.5 ± 1.5 $\mu g/m^3$ in PM_{10} (Table 1). This annual contribution is calculated as follows (*2*): the daily AD contribution is calculated, and for those days with AD contributions >0 $\mu g/m^3$ the AD contributions are subtracted from the PM_{10} values measured at the urban site. Subsequently, the urban data sets with and without corrections for AD contributions are averaged, and the difference between these averages is considered the annual mean AD contribution for Madrid.

TAU Method. The TAU method was not directly applicable to the Madrid data set given that the maximum PM_{10} hourly value recorded in 2007 was 145 $\mu g/m^3$ (lower than the 180 $\mu g/m^3$ threshold). Initially, we attempted to convert the two thresholds described in ref *5* (100 and 180 $\mu g/m^3$) into thresholds which could be applicable in Madrid, by decreasing them in proportion with the mean PM_{10} levels in Tel Aviv and Madrid. In this way, the characteristic thresholds for Madrid should have been 42 $\mu g/m^3$ (to be exceeded for at least 3 h) and 57 $\mu g/m^3$ (to be exceeded at least once during that period). However, when the algorithm was applied to

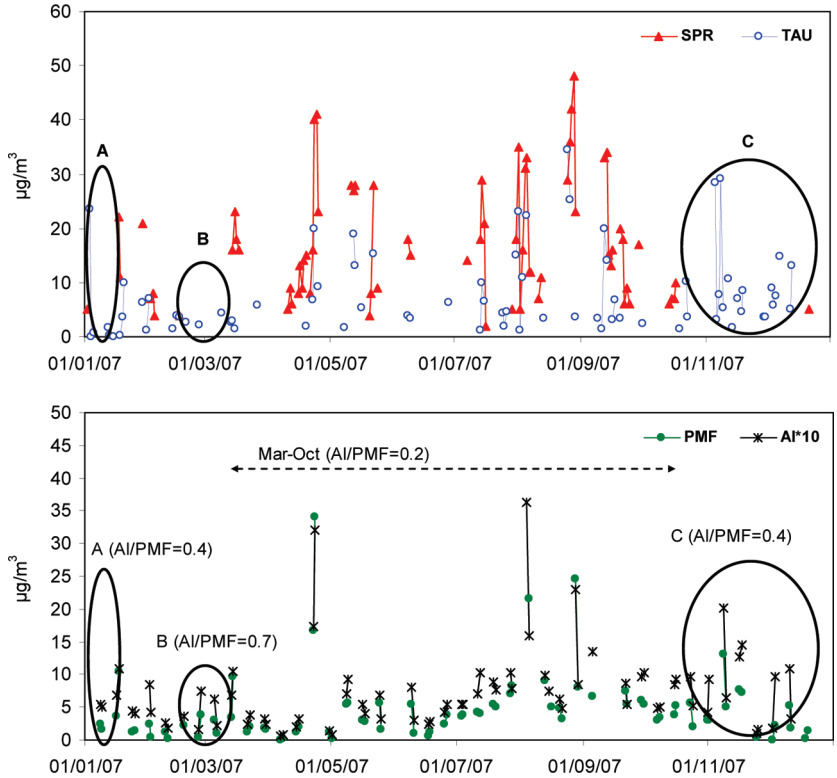

FIGURE 1. Top: Time series of African dust (AD) contributions to PM_{10} calculated by the SPR and TAU methods. Bottom: Time series of daily Al levels and of the AD source discriminated by PMF. Nonmatching events between the SPR and TAU methods are highlighted inside an ellipse.

TABLE 1. Number of Daily AD Episodes, Mean, Minimum, and Maximum Daily AD Contributions As Calculated by the SPR and TAU Methods, and by the PMF Receptor Model

African dust (AD)	SPR	TAU	PMF
number of daily episodes	71	81	81
mean annual contribution ($\mu g/m^3$)	3.5 ± 1.5	2.7	4.9 ± 0.5
maximum daily contribution ($\mu g/m^3$)	48	35	46
minimum daily contribution ($\mu g/m^3$)	2	1	1

the data using these thresholds, the AD events identified did not show an optimal correlation with levels of aluminum (Al) at the study site ($r^2 = 0.49$). A sensitivity analysis (described below) was carried out to determine appropriate thresholds for the Madrid data set. The best solution was achieved for a 35 $\mu g/m^3$ threshold to be maintained for at least 3 h, and an additional 58 $\mu g/m^3$ threshold. The selection of the best solution was based on the correlation between the daily AD levels obtained by the TAU method and the levels of Al.

By applying the TAU method with the newly defined thresholds, a total of 81 AD events were identified with daily contributions ranging between 1 and 35 $\mu g/m^3$ (Table 1). The annual mean contribution of AD to PM_{10} levels in 2007 was 2.7 $\mu g/m^3$, calculated as follows (*5*): a time period is defined by the number of half-hour records within *it nT*. For every half-hour *i* there is a PM_{10} concentration PM10*i*. The total PM10 during a time period is therefore

$$T = \sum_{i=1}^{nT} \mathrm{PM10}i$$

The average PM_{10} for a time period is

$$\mathrm{avg} = T/nT$$

During a time period one or more dust storms (DS) might be identified. The number of records during the DS or DS-s in a time period is *n*DS. The total PM_{10} during DS which occurred during a time period is therefore

$$\mathrm{TDS} = \sum_{i=1}^{n\mathrm{DS}} \mathrm{PM10}i$$

The average PM10 without DS is

$$\text{avg without DS} = \frac{T - \mathrm{TDS}}{nT - n\mathrm{DS}}$$

Therefore the contribution of DS to the average PM_{10} during this time period is

$$\text{DS contribution} = \text{avg} - \text{avg without DS}$$

Uncertainties could not be calculated for this method, although they are assumed to be those of the TEOM measurements. The time series of AD contributions calculated with the TAU method is shown in Figure 1 (top).

PMF. Seven emission sources were identified for PM_{10} using PMF, which included two mineral dust sources: local city dust (traced by Ca, Rb, Cs, Sn, Sb) and African dust (traced by Al_2O_3, K, Ti, Mn, Sr) (Figure S1, Supporting Information). Source contributions to the PM_{10} mass are shown in Figure S1, with a fit of $r^2 = 0.98$ between modeled and measured data (Figure S2, Supporting Information).

The two mineral dust sources showed similar chemical profiles (Figure S3, Supporting Information), but the main tracers of AD were detected typically linked to clay materials (Al, Ti), which are the main mineral components of AD (*8, 9*). The AD source showed a marked episodic character coin-

ciding with the occurrence of AD outbreaks over central Spain (Figure 1, bottom), with daily AD contributions ranging between 1 and 46 $\mu g/m^3$ (Table 1), and an annual AD contribution of 4.9 $\pm$ 0.5 $\mu g/m^3$ to mean annual PM_{10} (estimated uncertainty of 10% of the total load, calculated by applying a factor of 2 to the sum of the specific uncertainties of the major tracers of the source). The discrimination of the African dust source is especially relevant given that, to date, it had never been identified by receptor models in the >30 study locations in Spain where this same methodology was applied (*25*), due to collinearity constraints.

Aside from the discrimination of the AD source, one interesting result from the PMF analysis is the identification of a factor linked to residential coal combustion (marked by As and Se). In a large metropolis such as Madrid, residential coal combustion was expected to be negligible, especially in central heating systems. Residential coal combustion accounted for 9% of the mean annual PM_{10} mass.

Comparison between Methods. The results from the SPR and TAU show a relatively good agreement regarding the number of AD episodes detected and their magnitude on a daily level (minimum and maximum levels, Table 1). In total, the SPR method identified 71 days with contribution from AD, and 81 were identified by means of the TAU method. These are the days which should be reported to the Commission to be potentially discounted from the exceedances of the daily limit value (*1, 2*). As a result, based on the present data the TAU method would yield a larger number of potential discounts of the exceedances than the SPR method, which would be more conservative. The larger number of AD events reported by the TAU method results from the apparent misinterpretation of PM increments derived from local dust, as AD. The reason behind this misclassification is the fact that the TAU results are based on hourly measurements, which are more vulnerable to the influence of local sources than the 24 h measurements used by the SPR method. This interference with local sources only occurs during low impact AD events. In addition, the TAU method identified AD events on occasions where AD transport was not possible from a meteorological point of view. Due to the fact that meteorological scenario analysis is one of the bases of the SPR method, this misclassification is avoided.

The time series' of AD calculated by the SPR and TAU methods were compared with those obtained by PMF and with the daily mean levels of Al determined on the filter samples collected in Madrid. The levels of Al are markers of AD (*8, 9*), even if Al is not the only one (other tracers are Ti or Sr). On average, the daily AD episodes detected by the SPR and TAU methods coincided with the major AD events highlighted by the Al and PMF time series. Only during three periods were larger differences observed: (A) 01/03/2007−01/15/2007, (B) 02/13/2007−03/09/2007, and (C) 10/19/2007−12/13/2007, when AD was only detected by the TAU method. To interpret the atmospheric processes behind these periods, the ratio between the Al content and the AD source identified by PMF was calculated. The Al/PMF parameter was interpreted as an indicator of the presence of other sources of mineral dust, different from AD, given that the PMF model is able to distinguish AD from local or regional dust. Results showed clearly different ratios during these periods (0.4 $\pm$ 0.5 to 0.7 $\pm$ 0.5 standard deviation, Figure 1, bottom) and markedly different from the values obtained during the rest of the year (Al/PMF = 0.2 $\pm$ 0.1). This suggests that during the A, B, and C periods, the excess of Al originated from other sources of mineral dust in the study area, which were mistaken for AD. One possible interpretation is that, during winter time, local pollution episodes induced by strong anticyclonic atmospheric scenarios may be misinterpreted by the TAU method as AD events, given that hourly PM levels are increased during long periods of time (>10 h). These results evidence the ability of the TAU method to identify high-impact AD events, but also the clear need to adapt the thresholds in the algorithm to the specific aerosol levels at the location where it is applied, in order to refine detection of low-impact episodes. As shown by Ganor et al. (*5*), the TAU method provided less ambiguous results when applied to Tel Aviv data.

In terms of mass, the mean annual AD contributions to PM_{10} levels were in the same order of magnitude (SPR = 3.5 $\pm$ 1.5 $\mu g/m^3$, TAU = 2.7 $\mu g/m^3$, PMF = 4.9 $\pm$ 0.5 $\mu g/m^3$). The annual mean AD contributions calculated by the SPR and TAU methods were in good agreement with results found in the literature for Central Spain (3−4 $\mu g/m^3$, *14*), although the TAU result was slightly low. Conversely, the PMF result seemed to be relatively high in comparison with the SPR and TAU results and with other studies (*14*).

Finally, daily AD contributions by the SPR and TAU methods were plotted against Al levels and against AD contributions from the PMF model (Figure 2a and b). Results showed higher correlations between Al (main tracer of AD) and the daily AD contributions calculated by the SPR method ($r^2 = 0.72$, $y = 0.05x + 0.22$) than with the TAU method ($r^2 = 0.56$, $y = 0.06x + 0.66$). The same was true for the correlation with the PMF contributions of AD ($r^2 = 0.79$, $y = 0.65x - 1.45$ with SPR, and $r^2 = 0.43$, $y = 0.63 + 2.19$ with TAU). The daily AD contributions by the SPR and TAU methods were also correlated (Figure 2c). Results showed a moderate correlation between both sets of results ($r^2 = 0.58$), evidencing that both methods aim to estimate the same parameter but still differences are significant. The mean daily AD levels detected by the SPR method were somewhat lower than those by the TAU method, even if on an annual basis the opposite is true due to the fact that the mean annual AD contribution is calculated as the difference between the mean PM_{10} levels with and without AD contributions (see the Results and Discussion section, above). In addition, the correlation plot is unable to show the days for which a TAU AD contribution was detected, but no contribution was found with SPR. These are the low impact episodes described above (on average, AD < 5 $\mu g/m^3$), which are probably misclassified by the TAU method. Therefore, Figure 2c shows mainly the high impact episodes, which are generally identified by both methods.

In sum, it may be concluded that the SPR and TAU methods showed a good agreement in the general detection of the AD episodes. However, TAU method tended to assign an AD origin to low-impact events which, according to the present analysis, may be local or regional-scale dust contributions (and not strictly AD). This results in a larger number of AD events identified, which should be taken into account when evaluating the exceedances of the PM_{10} daily limit value. The number of exceedances at the Casa de Campo site was calculated for the year 2007 with the SPR and TAU methods. The overall number of exceedances of the 50 $\mu g/m^3$ daily limit value was 13 without taking into account AD contributions, and it decreased to 5 with the TAU method, and to 4 with SPR. Thus, both methods yielded very similar results. In this case, the difference was not larger because, even though the TAU method identified a higher number of events (81 vs 71 by SPR), their contribution in terms of mass was lower given that the 10 additional events were low impact ones, and therefore with a low mass contribution to be subtracted from the PM_{10} mass and resulting in a higher number of final exceedances.

Based on our results, we conclude that the SPR method is a more adequate tool for the identification and quantification of AD events than the TAU method. The main limitations detected were as follows: (a) for the TAU method, the fact that winter local pollution may be misinterpreted as AD events, and (b) for the SPR method, the fact that AD episode

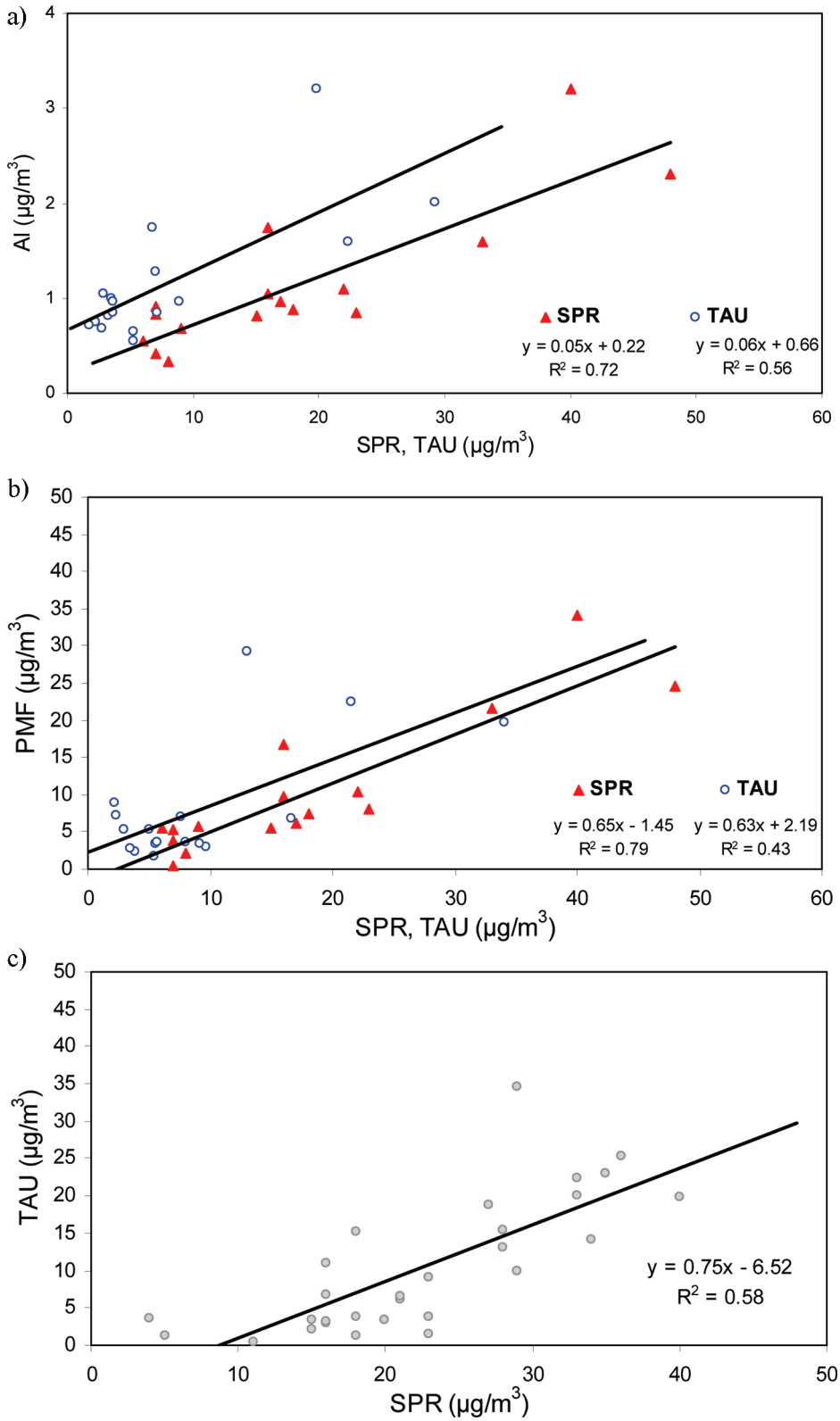

FIGURE 2. (a) Correlation between the mean daily levels of AI and the daily African dust (AD) contributions calculated with the SPR and TAU methods. (b) Correlation between the mean daily AD source discriminated by PMF and the daily AD contributions calculated with the SPR and TAU methods. The number of data points is limited by the sampling frequency of PM on filters, which was 2 samples per week. This results in a lower number of data points than those available with automatic instrumentation for the SPR and TAU calculations. (c) Correlation between daily AD contributions calculated with the SPR and TAU methods.

identification tools may imply a certain degree of subjectivity. Despite the good results obtained with Tel Aviv data, the application of the TAU method in other geographical locations requires its tuning to take into account specific aerosol levels.

Sensitivity Analysis. *SPR Method.* A sensitivity analysis of the SPR method was carried out with the aim to assess the robustness of the results delivered. One of the key determinants in the application of the SPR method is the selection of the reference regional background site for which the 30

days moving 40th percentile is calculated. In our study, the data from 4 stations (within an approximate 300 km radius, see Figure S4, Supporting Information) were analyzed: 2 EMEP stations (Peñausende and Risco Llano), and 2 regional background sites (Monfragüe and Atazar). The AD contributions were calculated for PM_{10} taking each site as reference and compared with the real reference site (Atazar) (Figure S5, Supporting Information).

The Atazar site is the correct reference site for the application of the SPR method due to proximity to the Madrid sampling station (65 km), as opposed to a minimum of 120 km and a maximum of 280 km distance from the remaining stations to the study area (Figure S5). The proximity of the Atazar site ensures that it is representative of the atmospheric transport processes registered in the Madrid airshed. The ratio between AD calculated at Peñausende, Monfragüe and Risco Llano and the one calculated at Atazar ranged between 64% and 67%. Thus, an inadequate selection of the reference station may result in the underestimation of AD by up to 36% in terms of mass. However, the AD ratio between sites does not increase linearly as the distance to Madrid decreases (Figure S5, Supporting Information): this is evidence that the distance between sites is simply a proxy for the ability of the reference site to represent the atmospheric conditions of the airshed at the study site. As an example, in Peñausende and Monfragüe the same result was obtained (2.3 $\mu g/m^3$, as opposed to 3.5 $\mu g/m^3$ in Atazar) despite the distance between these sites (200 km). Once again, the similar AD loads obtained are most probably a result of their location in the same airshed, along the characteristic pathway of February−March AD outbreaks registered over the Iberian Peninsula (*31, 36*).

As a result, the sensitivity analysis highlighted the relevance of the correct selection of the reference regional background station for the application of the SPR method.

TAU Method. As described above, the thresholds for the application of the TAU method in Madrid had to be redefined in order to adapt them to the mean PM_{10} levels and the impact of AD in the study area. Table S1 (Supporting Information) summarizes the 12 cases tested, including variations of both thresholds (thresholds 1 and 2) as well as of the minimum number of hours during which threshold 1 should be exceeded. Results show a large variability in the number of AD events (between 28 and 95), as well as in the correlation coefficients obtained in relation to Al ($r^2 = 0.03$ to 0.56). The optimal solution was estimated to be the one which maximized this correlation (case 5).

Acknowledgments

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Supporting Information Available

Figure S1 showing the source contributions to gravimetric PM_{10} mass resulting from the PMF analyses; Figure S2 showing the correlation between gravimetric and modeled PM_{10} mass, using PMF; Figure S3 showing the source profiles (g/g) of the mineral dust sources identified by PMF in PM_{10} for local city dust and African dust; Figure S4 showing the location of the regional background sites used in the sensitivity analysis of the SPR method (courtesy of Google Earth); Figure S5 showing the sensitivity analysis carried out for the SPR method; and Table S1 showing the sensitivity analysis carried out for the TAU method. This information is available free of charge via the Internet at http://pubs.acs.org/.

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