Estimating urban PM10 and PM2.5 concentrations, based on synergistic MERIS/AATSR aerosol observations, land cover and morphology data

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Abstract

This study evaluates alternative spatio-temporal approaches for quantitative estimation of daily mean Particulate Matter (*PM*) concentrations. Both fine (*PM*_{2.5}) and coarse (*PM*₁₀) concentrations were estimated over the area of London (UK) for the 2002–2012 time period, using Aerosol Optical Thickness (*AOT*) derived from MERIS (Medium Resolution Imaging Spectrometer) / AATSR (Advanced Along-Track Scanning Radiometer) synergistic observations at 1 km × 1 km resolution. Relative humidity, temperature and the K-Index obtained from MODIS (Moderate Resolution Imaging Spectroradiometer) sensor were used as additional predictors. High-resolution (100 m × 100 m) local urban land cover and morphology datasets were incorporated in the analysis in order to capture the effects of local scale emissions and sequestration. Spatial (2-D) and spatio-temporal (3-D) kriging were applied to in situ urban *PM* measurements to investigate their association with satellite-derived *AOT* while accounting for differences in spatial support. Linear mixed-effects models with day-specific and site-specific random intercepts and slopes were estimated to associate satellite-derived products with kriged *PM* concentration and their

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¹This article is dedicated to the memory of V.K. Klonias

predictive performance was evaluated.

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1. Introduction

Particulate Matter (*PM*) concentration of both fine (*PM*_{2.5}) and coarse (*PM*₁₀) particles is used as an air quality indicator in urban areas. Numerous studies, analysing the impacts of *PM* on human health, have found associations of *PM* with increased morbidity and mortality. Specifically, high *PM* loads in urban areas produced by local sources like transportation and industry (Katsouyanni et al., 2001), have been correlated with increased respiratory problems (Dimitrova et al., 2012), cardiovascular diseases (Franklin et al., 2006) and decreased birth weights and lengths (Ballester et al., 2010).

Monitoring of *PM* concentrations is primarily based on ground measurements. Despite the fact that dense station networks exist, in large cities like London, in situ measurements do not provide detailed information on the spatial distribution of *PM* at local scale. The temporal coverage of in situ *PM* measurements, which depends on the instrument operation period and functionality, is also highly variable. These reasons have prompted an ongoing effort for *PM* estimation using satellite observations. *PM* spatio-temporal distribution estimations derived by combined use of satellite observations, in situ measurements and numerical modelling was recently performed in five European cities, London included, in the framework of the FP7 project BRIDGE (Chrysoulakis et al., 2014 ; Borrego et al., 2011).

Aerosol Optical Thickness (*AOT*) is the most widely applicable satellite-derived product for the assessment of *PM* concentrations. *AOT* represents the integrated radiation scattering and absorption by aerosols in an atmospheric column from the surface to the top of the atmosphere; it is proportional to the number of airborne particles and, among other factors, depends on their mass concentration and size distribution. A variety of methods have been developed

for the estimation of *AOT* using spaceborne observations (e.g. Kokhanovsky, 2013), with the dark target approximation being the most widely used, as in the MODIS (Moderate Resolution Imaging Spectroradiometer) *AOT* products
 30 at $10\text{ km} \times 10\text{ km}$ (Levy et al., 2013) and $3\text{ km} \times 3\text{ km}$ (Remer et al., 2013) spatial resolution. Multi-angle algorithms have also been recently developed, such as the MERIS (Medium Resolution Imaging Spectrometer) / AATSR (Advanced Along-Track Scanning Radiometer) synergy algorithm (North et al., 2009) and the MAIAC (Multi-Angle Implementation of Atmospheric Correction)
 35 tion) algorithm (Lyapustin et al., 2011). These algorithms allow significant improvement in the *AOT* spatial resolution, which, at $1\text{ km} \times 1\text{ km}$ renders the product suitable for intra-urban *PM* studies.

Various techniques have been adopted to associate remotely sensed *AOT* with surface-measured *PM*. These include simple linear regression models
 40 between *AOT* and *PM* (Chu et al., 2003 ; Schaap et al., 2009 ; Wang and Christopher , 2003), multiple linear regression with additional covariates such as temperature, relative humidity, wind speed, boundary layer height (Gupta and Christopher, 2009a ; Benas et al., 2013b), chemical transport models (van Donkelaar et al., 2006 ; van de Kasstele et al., 2006) integrating satellite radi-
 45 ance (Drury et al., 2010 ; Wang et al., 2010), Generalized Linear Models (GLM) (Liu et.al, 2005, 2007), Artificial Neural Networks (ANN) (Gupta and Christopher, 2009b ; Wu et al., 2012), Generalized Additive Mixed (GAM) models (Liu et.al, 2009 ; Lee et al., 2012), Alternating Conditional Expectation (ACE) models (Benas et al., 2013b), Geographically Weighted Regression (GWR) (Song et
 50 al., 2014) and semi-empirical models (Lin et al., 2015).

Application of mixed-effects models with day-specific random intercepts and slopes (Lee et al., 2011) revealed that daily calibrations of satellite *AOT* data using ground *PM* measurements from a spatial monitoring network, provide substantially improved predictive power relative to static models. Furthermore,
 55 covariates such as Percent of Open Spaces, Elevation, Major Roads, Population Density and Meteorological variables, explained part of the spatial variability of *PM* concentrations within a day (Kloog et al., 2011 ; Nordio et al., 2013). Un-

fortunately such spatial predictors are in general difficult to obtain, or even unavailable for many areas of interest. Moreover, a limitation of previous studies is the coarse spatial resolution ($10\text{ km} \times 10\text{ km}$ and $3\text{ km} \times 3\text{ km}$) of *AOT* retrieved from MODIS sensor. In this work, the high-resolution $1\text{ km} \times 1\text{ km}$ *AOT* distributions derived by employing the MERIS/AATSR synergy algorithm developed by North et al. (2009) and validated by Benas et al. (2013a), were used. The Sky View Factor - *SVF* (Lindberg and Grimmond, 2010), accounting for the urban morphology and a post-classification of the Urban Atlas Land-Use/Cover - *LUC* (Urban Atlas, 2014) product are employed, to the best of our knowledge for the first time, to capture the spatial variability of *PM* concentrations within the study domain. These remotely-sensed spatial predictors are much easier to obtain in comparison with data used in previous works.

The present study uses data from multiple sources, measured at different spatial units. Combining such dissimilar data creates statistical challenges (Young et al., 2009) and leads to what is known as *the change of support problem*, which is concerned with valid inference regarding a spatial variable of one support (n -dimensional physical volume of the measured variable, including its geometric size, shape and spatial orientation) from data of different supports. Most research works that associate satellite-derived products with in situ *PM* concentrations do not focus on this issue: typically, areal data are used as point-referenced data by assigning the value of each pixel to the corresponding centroid. Unfortunately such practices may lead to aggregation bias as emphasized in the geostatistics literature (e.g. Armstrong, 1998, Gotway and Young, 2002). To address this issue, before associating satellite-derived products with in situ measurements, the latter were transformed using block-kriging, in accordance with the methodology presented in Young et al. (2009). The common geographical unit for analysis was selected to be $1\text{ km} \times 1\text{ km}$, matching the spatial resolution of the MERIS/AATSR derived *AOT*.

Benas et al. (2013b) applied kriging to homogenize in situ *PM*₁₀ measurements with satellite data with regard to their spatial scale. Nonetheless, simple kriging fails to account for local emission sources, such as the presence of in-

dustrial areas or highways between different monitoring stations, as well as for
90 local sequestration actors (e.g. urban green infrastructure). This article in-
vestigates whether incorporation of categorical *LUC* and *SVF* static datasets
could improve such limitations. The Urban Atlas *LUC* was expected to capture
emission sources, while the *SVF*, derived from a high spatial resolution Digital
Surface Model (DSM), was used as a proxy of the urban form (structure of the
95 three-dimensional urban surface) and was expected to explain the dispersion of
particles in the urban canopy.

Last, but not least, among the main objectives of this work was to develop
an operational tool capable to estimate high resolution *PM*₁₀ and *PM*_{2.5} con-
centration maps on a daily level, based only on satellite-derived products: high-
100 resolution $1\text{ km} \times 1\text{ km}$ *AOT* calculated by implementing the MERIS/AATSR
synergy algorithm, relative humidity, temperature, and the K-Index (which is
used as a proxy of the vertical aerosol mixing) from MODIS sensor. To this
end, mixed-effect models with a) day-specific and b) site-specific random effects
were estimated. The former are analogous to the “Stage 1” models presented
105 by Kloog et al. (2011) for estimation of *PM*_{2.5} and by Nordio et al. (2013)
for estimation of *PM*₁₀ particles, where the $10\text{ km} \times 10\text{ km}$ resolution *AOT*
from MODIS was used. The latter models are used for the first time, to in-
vestigate whether satellite-derived products can estimate *PM* concentrations in
areas where no daily in situ measurements are available.

110 2. Study area and datasets

Greater London roughly coincides with the built-up area of London, includ-
ing parts of the Metropolitan Green Belt. According to Eurostat, London is
the most populous city and metropolitan area of the European Union with a
population density of 4,761 people per square kilometre. London air quality is
115 continuously monitored at over 100 locations (London Air Quality Monitoring
Network, 2014), with particulate matter being measured at the majority of the
stations (Fig. 1 a); these stations formed the basis upon which the particular

study area was chosen. The UK Air Quality Standards Regulations sets standards (based on EU limit values) for a variety of pollutants considered harmful
120 to human health and the environment. Despite reductions for the majority of pollutants in the last years, the levels of *PM*₁₀ continue to exceed national air quality standards and objectives in some areas of London (Greater London Authority, 2014).

Hourly mean *PM*₁₀ and *PM*_{2.5} concentrations were obtained through the
125 *openair* open-source tool for the analysis of air pollution data (Carslaw and Ropkins, 2012), developed by the Environmental Research Group at King’s College London and supported by the University of Leeds. Hourly data were used to calculate average daily *PM* concentrations. The study period was selected to be 2002-2012, in order to match with the available MERIS and AATSR
130 observations. All data was converted to the Lambert Azimuthal Equal Area (ETRS89-LAEA5210) projection, recommended by the European Environment Agency (EEA, 2006) for storing raster data, statistical analysis and map display purposes.

The MERIS/AATSR synergy algorithm for aerosol retrieval (North et al.,
135 2009), available in the BEAM software toolbox of the European Space Agency (Brockmann Consult, 2011), was used to derive the *AOT* distribution. To this end, a java-based code was implemented to automatically produce *AOT* values for the whole 2002 – 2012 time period, as well as to adjust and reproject the results to our study area. An advantage of the synergy is that it provides *AOT*
140 values at a $1\text{ km} \times 1\text{ km}$ spatial resolution in comparison to the $10\text{ km} \times 10\text{ km}$ given by MODIS. Figure 1(b) illustrates an example of the synergy derived *AOT* product; a fixed $1\text{ km} \times 1\text{ km}$ grid was created to be a common geographical unit for all further analyses.

Another advantage of the MERIS/AATSR synergy is that aerosol data are
145 provided in case of high-surface reflectance, where MODIS *AOT* retrieval algorithm fails. This is due to the dual view geometry of the synergy algorithm: while in single-view methods the separation of the surface contribution to the sensor measurement is based on a priori assumptions (e.g. the dark target ap-

proximation, Remer et al., 2005), use of multiple view-angle imagery allows an
150 additional constraint to be placed, since the same area is viewed through different atmospheric path lengths. Hence, no a priori information of the surface spectrum is required, and aerosol properties can be retrieved over all surface types (North et al., 2009).

The main sources of error in the final AOT product are related to algorithm
155 retrieval, instrument calibration, interpolation and the radiative transfer model (North et al., 2009). The MERIS/AATSR synergy algorithm in addition to AOT values provides AOT uncertainty (AOTU) maps. In the dataset analyzed here, most AOTU values (approx. 90%) were less than 0.5, with the vast majority close to 0, the lowest level of uncertainty. More than 1% of these data take very
160 large values (> 10000); these are mostly due to the algorithm retrieval errors and therefore considered as outliers. The analyses presented in the next sections are based on AOT data for which $AOTU < 0.5$; this threshold was chosen by a sensitivity analysis of the predictive performance of mixed-effects models.

A disadvantage of the synergy algorithm, is the coarse temporal resolution
165 of the MERIS and AATSR observations, which were simultaneously acquired over Greater London just once per day, in the time window between 10:30 and 11:00 UTC. In contrast, MODIS on-board both Terra and Aqua platforms is able to perform a morning and an afternoon acquisition each day. Thus, the average of the MODIS-derived *AOT* from these two acquisitions is expected to
170 be closer to the daily mean values. Moreover, MODIS daily observations are more frequent within a year relative to MERIS/AATSR.

The European Urban Atlas *LUC* is part of the local component of the
GMES/Copernicus land monitoring services. Satellite imagery has been used to create reliable high-resolution maps of urban land in a cost-efficient manner.
175 It provides data related to transport, environment and land use for Large Urban Zones with more than 100,000 inhabitants as defined by the Urban Audit. Figure 2(a) illustrates the polygon-shaped $4\text{ m} \times 4\text{ m}$ resolution *LUC* map for the Greater Area of London, which includes 20 distinct classes.

SVF is the fraction of sky visible when viewed from the ground up. It is a

180 dimensionless variable that ranges from 0 to 1. A value of 1 denotes that the sky is completely visible, i.e. in a flat terrain; when a location has buildings or trees SVF decreases proportionally. For the calculation of SVF the Relief Visualization Toolbox Computation, version 1.0 (Zakšek et al., 2011) was used to analyze a lidar-derived high spatial resolution DSM. The DSM was made
185 available by the Greater London Authority in the framework of the BRIDGE Project (Chrysoulakis et al., 2013). The resulting raster map has a $4\text{ m} \times 4\text{ m}$ resolution (Fig. 2 b). SVF is a remote sensing product; in our analyses it was adopted as an alternative to the more commonly used “Percent of Open Spaces” covariate (e.g. used in Kloog et al., 2012).

190 Atmospheric temperature and relative humidity profiles at 20 pressure levels ($1000\text{hPa} - 5\text{hPa}$), as well as surface pressure, were retrieved from the MODIS Level 2 Atmospheric Profile Product for the period examined (2002-2012). Surface Temperature ($STMP$) and Relative Humidity ($RHUM$) were estimated using linear interpolation or extrapolation of atmospheric profiles and corre-
195 sponding surface pressure data. The K-Index - $KIND$ (George , 1960), an atmospheric static stability estimator, was used as an indicator of the corresponding aerosol vertical mixing height as in Benas et al. (2013b). The aforementioned data, available on a daily basis and at $5\text{ km} \times 5\text{ km}$ spatial resolution, were reprojected to the geographical system of the study and resampled to our
200 $1\text{ km} \times 1\text{ km}$ grid using bilinear interpolation. Hence, it was assumed that the variability of these data is small within the $5\text{ km} \times 5\text{ km}$ grid; we acknowledge the limitation of this approach, particularly in the case of $RHUM$.

3. Model Development Methodology

To address the *change of support problem* all data was brought to the same
205 spatial resolution, selected to be $1\text{ km} \times 1\text{ km}$, which is the resolution of the satellite-derived AOT . To this end, in situ PM were interpolated using spatial - 2-D and spatio-temporal - 3-D kriging (discussed in Sect. 3.2). Thus, $100\text{ m} \times 100\text{ m}$ blocks were obtained and the resulting surface was up-scaled to

a $1 \text{ km} \times 1 \text{ km}$ grid, by averaging per each 10×10 cell. To exploit the high
210 spatial resolution of *LUC* and *SVF*, interpolation was applied to the residuals
of the multiple linear regression model, which used these variables as predictors.
Finally, the predictive capability of linear mixed-effects models (Sect. 3.3 and
3.4) with day-specific and site-specific random effects was evaluated. Figure 3
illustrates a graphical representation of the adopted procedure. In what follows
215 the estimation procedure is presented in full detail for *PM*₁₀; the same steps
were applied for the estimation of *PM*_{2.5}.

3.1. *LUC* & *SVF* - *PM* Relationship

Average daily *PM* concentrations are expected to vary for different *LUC*
classes. To better understand the urban surface characteristics that surround
220 *PM* stations, a buffer zone of $100 \text{ m} \times 100 \text{ m}$ around each station point was
created. Then, the *LUC* map was clipped with these buffer zones and the
dominant *LUC* category within each buffer zone was assigned to the respective
PM site (Fig. 4 a). The resulting land cover classes (LUC_k , $k = 1, \dots, 10$)
and the average *PM* concentrations per class are presented in Table 1.

To perform pairwise comparisons of the *PM* concentrations means across
*LUC*_{*k*} classes, the pairwise comparisons method for unequal sample sizes, known
as *Tukey's* method, was performed. This approach can be applied simultane-
ously to all comparisons $\{LUC_k - LUC_l\}$; it is based on the *studentized range*
distribution $q_{r,s}$ with *r* and *s* degrees of freedom. The null hypothesis postulates
equal population means; given *I* samples, denoting by x_L and x_S the largest
and smallest sample means respectively, by n_L and n_S the corresponding sample
sizes and by *N* the total sample size, the test statistic is formulated as:

$$\frac{x_L - x_S}{\sqrt{(\frac{MSE}{2})(\frac{1}{n_L} + \frac{1}{n_S})}} \sim q_{I, N-I}. \quad (1)$$

Using this test statistic, the null hypothesis $H_0 : LUC_k - LUC_l = 0$ versus the
alternative $H_1 : LUC_k - LUC_l \neq 0$ for $k, l = 1, \dots, 10$, $l > k$ was tested. LUC_k
and LUC_l are significantly different at level α if:

$$|\bar{x}_k - \bar{x}_l| \geq q_{I, N-I, 1-\alpha} \sqrt{(\frac{MSE}{2})(\frac{1}{n_L} + \frac{1}{n_S})} \quad (2)$$

225 The resulting p -values are presented in Table 2. Six land-cover classes were
 formed based on statistically significant differences between means of PM_{10}
 concentrations:

1. Agricultural - Semi-natural areas - Wetlands
2. Sports and leisure facilities
- 230 Green urban areas
3. Airports
 - Discontinuous Medium Density Urban Fabric (S.L. : 30% - 50%)
 - Discontinuous Dense Urban Fabric (S.L. : 50% - 80%)
4. Industrial, commercial, public, military and private units
- 235 5. Port areas
 - Other roads and associated land
6. Continuous Urban Fabric

The classification procedure was unclear for “Port areas” which was not signifi-
 cantly different from most other classes, due to small sample size. This category
 240 was grouped with “Other roads and associated land”, since the largest p -value
 ($=0.999$) of the hypothesis testing procedure was found for the comparison of
 these two classes. Furthermore, since the initial set of classes provided by the
 Urban Atlas LUC Map was too large (20 classes), in order to get estimates for
 the whole area, classes with no in situ observations were merged with the above
 245 six groups. The final categorization is presented in Table 3 and the merged land
 cover raster map is shown in Fig. 4(b).

After land cover classes were merged, a linear regression with LUC -specific
 intercepts and SVF as a continuous predictor was applied to log-transformed
 average daily PM_{10} concentrations:

$$\log(PM_{ij}) = \alpha_0 \cdot SVF_i + \sum_{k=1}^6 \alpha_k \cdot \mathbb{1}(LUC_i = k) + \epsilon_{ij}, \quad i = 1, \dots, M, \quad j = 1, \dots, n_i \quad (3)$$

where PM_{ij} denotes PM concentration observed at measurement site i on day
 j , LUC_i and SVF_i represent LUC category and SVF at site i , ϵ_{ij} represents

the error term, which is assumed to be independently distributed as $\mathcal{N}(0, \sigma^2)$,
 250 M denotes the number of spatial PM sites and n_i is the number of days with
 available observations at site i .

SVF and LUC were statistically significant explanatory variables ($p < 0.001$
 for all t statistics). Notably, the estimated coefficient for SVF in Eq.3 was neg-
 ative, which is in accordance with prior expectations: higher levels of sky view
 255 factor are associated with high dispersion potential of particulate matter in the
 atmosphere which is expected to result in reduced PM concentrations observed
 at that particular location. Thus, interpolation of the residuals obtained from
 Eq.3 was performed, in addition to kriging of raw and log transformed data.
 The logarithmic transformation was adopted in Eq.3, as residuals of the trans-
 260 formed data follow a normal distribution reasonably well (Fig.5 b and c), in
 contrast with raw PM concentrations which were right skewed (Fig.5 a). In-
 ferences (confidence intervals and hypothesis tests) on conventional regression
 and mixed-effects models that will be presented in the next sections, are based
 on the normality assumption. It is also worth noting that the transformation
 265 was beneficial for the predictive power of mixed-effects models that will be dis-
 cussed next; this was verified via cross-validation but results are not presented
 for brevity.

3.2. Kriging

Kriging is a statistical model that can describe how PM varies in space,
 270 based on in situ concentrations. In this work, kriging was applied primarily
 to address the difference in spatial support of in situ PM and satellite-derived
 predictors. The latter were not associated with the original PM data which
 were of point support, but with their block-kriged counterparts, in accordance
 with the methodology presented in Young et al. (2009). Kriging predicts unob-
 275 served values of the random process $Z(\cdot)$ from data observed at known locations
 $\{\mathbf{s}_1, \mathbf{s}_2, \dots, \mathbf{s}_n\}$. Using $\mathbf{Z} = (Z(\mathbf{s}_1), \dots, Z(\mathbf{s}_n))^T$ to represent PM concentra-
 tions at points of $D \subset \mathbb{R}^d$, the predictor of $Z(\cdot)$ at a point $\mathbf{s}_0$ is denoted by
 $p(\mathbf{Z}; \mathbf{s}_0)$. *Ordinary Kriging* (Cressie, 1993) refers to spatial predictor under the

following two assumptions:

1. Model Assumption

$$Z(\mathbf{s}) = \mu + \delta(\mathbf{s}), \quad \mathbf{s} \in D, \mu \in \mathbb{R}, \quad \text{and } \mu \text{ unknown.} \quad (4)$$

2. Predictor Assumption

$$p(\mathbf{Z}; \mathbf{s}_0) = \sum_{i=1}^n \lambda_i Z(\mathbf{s}_i), \quad \sum_{i=1}^n \lambda_i = 1. \quad (5)$$

The condition that coefficients sum to 1 guarantees uniform unbiasedness, i.e.

$$E[p(\mathbf{Z}; \mathbf{s}_0)] = E\left[\sum_{i=1}^n \lambda_i Z(\mathbf{s}_i)\right] = \mu \quad \text{for all } \mu \in \mathbb{R} \quad (6)$$

and an optimal predictor $p(\cdot; \mathbf{s}_0)$ is derived by minimizing mean-squared prediction error

$$\sigma_e^2 = E\left[Z(\mathbf{s}_0) - p(\mathbf{Z}; \mathbf{s}_0)\right]^2 \quad (7)$$

280 over $(\lambda_1, \dots, \lambda_n)$, subject to $\sum_{i=1}^n \lambda_i = 1$.

The need for models that interpolate PM based on valid space-time covariance structures has been highlighted in Liu et.al (2009). Following Gräler et al. (2011) and Gräler et al. (2013), where the potential of different approaches for spatio-temporal interpolation of PM_{10} concentrations was investigated, this work evaluated two alternative methods: 2-D - *ordinary kriging* using separate daily variograms and 3-D - *metric kriging*. In the first case the semivariogram is defined as:

$$\gamma(\mathbf{h}) = \frac{1}{2} \cdot \mathbb{E}\left[Z(\mathbf{s}) - Z(\mathbf{s} + \mathbf{h})\right]^2 \quad (8)$$

where $\mathbf{s} = (x_1, x_2)$, with x_1 representing Northing and x_2 Easting. Thus, in this case spatial dependence patterns are allowed to change on a daily basis. 3-D kriging extends the 2-dimensional geographical space to a 3-dimensional space-time environment. Hence, PM is described as a function of x_1 , x_2 and time t :

$$Z = Z(x_1, x_2, t) = Z(\mathbf{s}, t) \quad (9)$$

with the semivariogram:

$$\gamma(\mathbf{h}, \Delta) = \frac{1}{2} \cdot \mathbb{E} \left[Z(\mathbf{s}, t) - Z(\mathbf{s} + \mathbf{h}, t + \Delta) \right]^2. \quad (10)$$

To obtain meaningful results from isotropic covariance models in 3-D kriging, the temporal domain had to be rescaled to match the spatial one. Since the number of stations and the locations of stations measuring *PM* were changing from year to year, the scaling parameter that influences the spatio-temporal covariance had to be determined for each year separately. To this end, a procedure similar to the one proposed in Gräler et al. (2013) was followed. First, pure spatial and pure temporal *pooled* (Gräler et al., 2011) variograms were estimated and a heuristic scaling parameter was computed taking the fraction of both. Then a vector of scales ranging from 10 *km/day* to 20 *km/day* with a 500 *m/day* step (suggested from the previous results) was created, and the optimal scale was selected by leave-one-station-out cross-validation: the data of one validation site was separated from the training sites and the model was developed based on the training sites to predict PM concentrations at the validation site. This process was repeated until each of the spatial locations was tested (exactly once). The following performance metrics were examined: Mean Error (*ME*), which is a measure of bias, Root Mean Square Error (*RMSE*), Mean Absolute Error (*MAE*) and Pearson’s Correlation Coefficient (*R*).

In 3-D kriging, interpolation is not restricted to single time slices, since estimation is based on a selected maximum number of nearest neighbours in the space-time cube. In the present study, four maximum values (10, 100, 500 and 1000) of neighbours were evaluated. The above procedure was repeated for 3 widely used semivariogram forms: spherical, exponential and Gaussian. Finally, average concentrations per (100 *m* × 100 *m*) block were computed by *block kriging* (Cressie, 1993): a fine grid was placed across each block and ordinary kriging was used to estimate values at each point on the grid. Then, estimated values at grid points within each block were averaged, to obtain the estimated value for the whole block. The aforementioned method has been used in previous works to associate data with different spatial supports (i.e. Gotway and Young, 2002).

A disadvantage of the adopted method is the assumption of a metric covari-
 310 ance model that neglects the distinction between spatial and temporal domains.
 An advantage is that it handles easily missing data at any location for a given
 day, using information from the previous and the following days. Furthermore,
 it can be applied to a small number of in situ observations, which was the
 case for $PM_{2.5}$ concentrations. In this case, 2-D kriging resulted in singular
 315 variogram models, which neglect spatial dependencies.

Raw and log-transformed data, as well as residuals computed from Eq.3
 were interpolated to obtain an estimated average value for each $100\text{ m} \times 100\text{ m}$
 block surrounding a particular PM station. In general, the kriging predictor
 is asymptotically unbiased and gives the correct estimate when applied to raw
 PM concentrations. When applied to log-transformed PM , $Y(\mathbf{s})$ were back-
 transformed using the equation:

$$Z(\mathbf{s}) = \exp \left(Y(\mathbf{s}) + \frac{\sigma^2(\mathbf{s})}{2} \right) \quad (11)$$

with $\sigma^2(\mathbf{s})$ denoting the bias-correction factor (Denby et al., 2008). When resid-
 uals are interpolated, $Y(\mathbf{s})$ represents the estimate which combines regression
 predictions with kriged residuals. $Z(\mathbf{s})$ represents estimated PM concentra-
 tions at a $100\text{ m} \times 100\text{ m}$ resolution, denoted by $PM[kriged]$ in the following.
 320 Finally, to comply with the MERIS/AATSR synergy derived AOT , the kriged
 $100\text{ m} \times 100\text{ m}$ surface was up-scaled at $1\text{ km} \times 1\text{ km}$ resolution averaging for
 every 10×10 cell.

3.3. Linear Mixed-Effects Models: day-specific random effects

Data homogenization with regard to spatial support and geographic projec-
 325 tion was followed by an evaluation of the predictive capability of Linear Mixed-
 Effects Models with day-specific random effects ($LMM1$). This model class
 was proposed in Lee et al. (2011) to better capture the large daily variability
 in the $AOT - PM$ relationship. In this article $LMM1$ was based on the fol-
 lowing satellite-derived predictors: the high-resolution MERIS/AATSR synergy
 330 derived AOT product, $KIND$ and meteorological variables $STMP$, $RHUM$.

Satellite-derived covariates displayed clear seasonal patterns; in order to work with data which is stationary in mean (Cowpertwait and Metcalfe, 2009), for each covariate, deviations from its estimated annual profile were computed. Annual profiles were estimated by fitting a sinusoid to the time series:

$$E[X(t)] = a + b \cdot \sin\left(\frac{2\pi}{365.25}(t + t_0)\right) \quad (12)$$

where t is the Julian Day of the year, $X(t)$ denotes observed *AOT*, *STMP*, *RHUM* or *KIND* at day t , and a, b, t_0 denote unknown coefficients.

Figure 6 depicts estimated seasonal profiles using Nonlinear Least Squares (NLS) and Nonlinear Absolute Deviations (NAD) together with the derived equations for the NLS case. The performance of median regressions (which corresponds to NAD) was similar to the one achieved by conventional mean regression which suggests the absence of outlying measurements. Moreover, since deviations from annual profiles, denoted by *DevAOT*, *DevSTMP*, *DevRHUM* and *DevKIND*, were better explaining the variability of *PM* in the performance evaluation of mixed-effects models, further analyses refer to them.

The model-building procedure for mixed-effects models decides which coefficients need random effects to account for their between-day variation and which coefficients can be treated simply as fixed effects. In the analyses presented in the following sections, the protocol proposed in Pinheiro and Bates (2006) and Zuur et al. (2009) was adopted. Comparisons between models with different random effects structures was based on Anova tests, as well as on the Akaike (AIC) and the Bayesian Information Criteria (BIC). The interested reader may consult Pinheiro and Bates (2006) and Zuur et al. (2009) for further details on model building and estimation of mixed effects models. The general model is based on the following formulation:

$$\begin{aligned} \log(PM[kriged]_{ij}) = & (\beta_0 + b_{0,j}) + \beta_{0,k}MO_k + \beta_{0,l}DW_l + (\beta_1 + b_{1,j})DevAOT_{ij} + \\ & + (\beta_2 + b_{2,j})DevSTMP_{ij} + (\beta_3 + b_{3,j})DevRHUM_{ij} + (\beta_4 + b_{4,j})DevKIND_{ij} + \epsilon_{ij} \end{aligned} \quad (13)$$

$$\text{with: } \begin{pmatrix} b_{0,j} \\ b_{1,j} \\ b_{2,j} \\ b_{3,j} \\ b_{4,j} \end{pmatrix} \sim \mathcal{N} \left(\begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \mathbf{\Psi} \right) \quad \text{and} \quad \epsilon_{ij} \sim \mathcal{N}(0, \sigma^2),$$

where $PM[kriged]_{ij}$ denotes block-kriged PM concentration observed at spatial site i on day j , $DevAOT_{ij}$, $DevSTMP_{ij}$, $DevRHUM_{ij}$, $DevKIND_{ij}$ represent respectively, deviations from the seasonal profiles of AOT , $STMP$, $RHUM$, and $KIND$, at site i on day j , β_0 and $b_{0,j}$ correspond to coefficients for the fixed and random intercepts, whereas $\beta_1, \beta_2, \beta_3, \beta_4$ and $b_{1,j}, b_{2,j}, b_{3,j}, b_{4,j}$ denote the fixed and random slopes, respectively. MO_k and DW_l are dummy variables for months and days of the week ($k = 2, \dots, 12$ and $l = 1, \dots, 7$), with $\beta_{0,k}$ and $\beta_{0,l}$ denoting the corresponding coefficients. $\mathbf{\Psi}$ is the variance-covariance matrix for the day-specific random effects and ϵ_{ij} represents the error terms. The full general model included all 2-way interactions of the fixed-effects which are omitted in Eq.13 for brevity.

The fixed effects $\beta_0 - \beta_4$, $\beta_{0,k}$ and $\beta_{0,l}$ in Eq.13 represent the mean values of model parameters. $LMM1$ focuses on temporal instability in the association between satellite-derived and in situ measurements: day-specific deviations are represented by the random effects $b_{0,j} - b_{4,j}$, which are assumed to follow a multivariate normal distribution characterized by $\mathbf{\Psi}$. Random effects corresponding to different days are assumed to be independent; this is a limitation of $LMM1$. Day-specific errors ϵ_{ij} are assumed to be normally distributed and independent of the random effects.

3.4. Linear Mixed-Effects Model: site-specific random effects

$LMM1$ is based on daily PM measurements and cannot be used to produce PM maps in days which lack in situ measurements, as the corresponding random effects cannot be estimated. To address this issue, Linear Mixed-Effects Models with site-specific random effects (dubbed $LMM2a$) were developed and their predictive capability was evaluated. $LMM2a$ focuses on spatial instability in the

association between satellite-derived and in situ measurements: random effects correspond to site-specific deviations from the mean value of the coefficients. In this case, it is the available measurement positions that are treated as a sample from a population.

The model-building procedure applied for *LMM1* was performed again, to evaluate fixed and site-specific random effects; furthermore, auto-correlated location-specific errors were taken into account. Due to a large number of missing days with available satellite-derived products, leading to in situ measurements not equally spaced in time, a continuous autoregressive structure was used. This structure fits a continuous first-order autoregressive process: the correlation between errors $\epsilon_{i,t}$ and $\epsilon_{i,t+\Delta t}$ observed at location i is expressed as $\rho(\Delta t) = \phi^{|\Delta t|}$, with $0 \leq \phi < 1$ (Pinheiro and Bates, 2006). The general model was based on the following formulation:

$$\log\left(PM[kriged]_{ij}\right) = (\beta_0 + b_{0,i}) + \beta_{0,k}MO_k + \beta_{0,l}DW_l + (\beta_1 + b_{1,i})DevAOT_{ij} + (\beta_2 + b_{2,i})DevSTMP_{ij} + (\beta_3 + b_{3,i})DevRHUM_{ij} + (\beta_4 + b_{4,i})DevKIND_{ij} + \epsilon_{ij} \quad (14)$$

with: $\begin{pmatrix} b_{0,i} \\ b_{1,i} \\ b_{2,i} \\ b_{3,i} \\ b_{4,i} \end{pmatrix} \sim \mathcal{N}\left(\begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \Psi\right)$ and $\epsilon_{i,j} = \phi_1 \cdot \epsilon_{i,j-\Delta t} + a_{ij}$, where $a_{ij} \sim \mathcal{N}(0, \sigma^2)$

370

$\beta_0 - \beta_4$, $\beta_{0,k}$ and $\beta_{0,l}$ represent mean values of the parameters in the population of measurement sites. The random effects $b_{0,i} - b_{4,i}$ account for location-specific deviations in the association between satellite and in situ measurements and are assumed to follow a normal distribution with variance-covariance matrix Ψ .

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Again, the full model included two-way interactions of the covariates which are not shown.

In Eq.14, the K-Index, an atmospheric static stability estimator, was used as a continuous covariate. In previous studies it has been used as a categorical

variable (e.g Chrysoulakis et al., 2004 ; Benas et al., 2013b). Therefore, another model (labeled *LMM2b*) was tested, using the K-Index as a dichotomous indicator of aerosol vertical mixing height. Specifically, a 2-regime model with site-specific random intercepts and random slopes was tested. The first regime was corresponding to atmospheric static instability (suggested by high values of the K-Index) and the second was related to static stability (low K-Index values). To estimate the optimal value of *KIND* that separates the two regimes, a threshold regression model (Hansen, 2000) was estimated:

$$PM[krigged]_{ij} = \begin{cases} \beta_{0S} + \beta_{S,k}MO_k + \beta_{S,I}DW_i + \beta_{1S}DevAOT_{ij} + \beta_{2S}DevSTMP_{ij} + \beta_{3S}DevRHUM_{ij}, & \text{if } KIND_{ij} < th \\ \beta_{0I} + \beta_{I,k}MO_k + \beta_{I,I}DW_i + \beta_{1I}DevAOT_{ij} + \beta_{2I}DevSTMP_{ij} + \beta_{3I}DevRHUM_{ij}, & \text{if } KIND_{ij} \geq th \end{cases} + \epsilon_{ij} \quad (15)$$

where *S* corresponds to the static stability, *I* corresponds to instability and *th* represents the estimated threshold. Again, two-way interactions were included in the fixed effects part and site-specific random terms were evaluated using the forward stepwise procedure which takes into account auto-correlated location-specific errors.

5-fold cross validation was performed to gauge the quality of both mixed-effect models: the dataset was repeatedly randomly divided into 80% (training set) and 20% (test set) splits; predictions for the test set were made using the estimated model from the training set. Moreover, leave-one-pixel-out cross-validation was applied to evaluate the generalization capability of the model to any grid-cell of the study domain. This evaluation is similar to leave-one-station-out, described in the previous section for kriging. The difference is that instead of in situ measurements, block-kriged *PM* concentrations at pixels that contain measurement stations were used. In all cross-validation experiments, the out of sample predictive performance was evaluated based on R^2 , *ME*, *MAE*, mean (*MAPE*) and median (*MDAPE*) absolute percentage errors.

4. Results and Discussion

4.1. Descriptive Statistics

Table 4 presents average annual *PM*10 and *PM*2.5 concentrations measured at London’s Air Quality stations during the 2002 – 2012 study period, and the

number of measurement stations per year. Average annual PM_{10} concentrations ranged from $24.91 \mu g m^{-3}$ in 2010 to $32.04 \mu g m^{-3}$ in 2003 and $PM_{2.5}$ concentrations ranged from $13.59 \mu g m^{-3}$ in 2002 to $16.18 \mu g m^{-3}$ in 2007. The
400 number of stations that provide $PM_{2.5}$ quintupled from 2002 to 2012 whereas the number of stations that provide PM_{10} ranged from 52 in 2002 to 77 in 2006.

Though, as mentioned above, the particular study domain was chosen for its dense in situ PM measuring stations network, the main disadvantage of this
405 area is the large percentage of missing satellite-derived AOT observations due to cloud cover, especially in winter. Another drawback is the poor temporal resolution of the MERIS and AATSR sensors (one acquisition per 2-3 days). Both these reasons, combined with the algorithm's quality criteria, resulted in valid data for 358 days for the 11-year study period. The average daily AOT
410 values varied from 0.03 to 0.77 with higher values in the warm season and lower in the cold season.

The results of any statistical estimation technique should be interpreted in the context of the uncertainty and variability of the estimated products. In our case, two sources of uncertainty had to be considered: the first was caused by the
415 estimation of areal PM concentrations from in situ measurements using kriging, that led to the use of estimated values instead of observed PM concentrations in the regression model. The second source of uncertainty was caused by estimation of the regression coefficients in the mixed-effects models. In the following, we present results separately for each source of uncertainty.

420 4.2. Estimation of PM_{10}

4.2.1. Kriging

2-D kriging relied on a day-specific variograms, whilst 3-D metric kriging relied on a single variogram per year. Preliminary investigations based on cross-validation suggested that the spherical variogram (Eq.16) captured spatial and spatio-temporal dependencies more effectively, compared to exponential and

Gaussian variograms; therefore, it was adopted in all further analyses:

$$\gamma(\mathbf{h}) = ps \cdot \left(\left(\frac{3\|\mathbf{h}\|}{2r} - \frac{\|\mathbf{h}\|^3}{2r^3} \right) \mathbf{1}_{(0,r)}(\|\mathbf{h}\|) + \mathbf{1}_{[r,\infty)}(\|\mathbf{h}\|) \right) + n \mathbf{1}_{(0,+\infty)}(\|\mathbf{h}\|) \quad (16)$$

The parameters ps (Partial Sill), n (Nugget) and r (Range) in Eq.16 were estimated using the R-package *gstat* (Pebesma, 2004). The results of leave-one-station-out cross validation in case of 2-D ordinary kriging are summarized in
425 Table 5. The best performing method is based on interpolation of the residuals obtained from multiple regression of log-transformed PM_{10} . For 3-D kriging, the best performance in the cross-validation experiment, was achieved by taking at most 100 neighbours to estimate PM at a given location. The outcome was markedly inferior for 10 neighbours, whereas the use of 500 and 1000 neigh-
430 bours showed small improvements, increasing immensely computational time. The estimated variogram parameters, the scales that resulted in optimal cross-validation results (on a daily level) and the corresponding performance metrics are presented in Table 6. Annual differences in estimated parameters are influenced by changes in the number of available measurements per air quality
435 station, and the variability in distances between these stations.

Results are similar to the ones presented in Gräler et al. (2011) and Gräler et al. (2013), outperforming them for some years, which should be expected since in the present study metric-kriging was applied at a completely different scale, having much smaller spacing distance between pairs of stations. Another
440 explanation is the use of *LUC* and *SVF* static datasets in multiple regression, which aimed to account for local emission, sequestration and diffusion of the particles. Cross-validation results suggest that 3-D kriging outperformed 2-D kriging only in terms of bias. The levels of accuracy achieved from 3-D kriging were close to the ones achieved using daily variograms, leading to a smoother
445 PM kriged surface and thus being closer to the satellite observations at $1 \text{ km} \times 1 \text{ km}$. Moreover, the large local variability observed in PM_{10} concentrations and the small number of in situ stations measuring $PM_{2.5}$, resulted in singular daily variogram models. Therefore, in the estimation of mixed-effects models that will follow, interpolated values using 3-D kriging were used.

Block kriging was applied to the outcomes of 3-D kriging to estimate average PM concentrations at every $100\text{ m} \times 100\text{ m}$ cell. The resulting surface was upscaled to $1\text{ km} \times 1\text{ km}$ spatial resolution by computing the mean value for every 10×10 block. Figures 7(a) and 7(b) show an example of kriged PM_{10} surface for the whole study area, before and after upscaling; in this case no information from satellite-derived products was used. In Figure 7(a) one may observe the effect of LUC and SVF on the spatial distribution of PM concentrations: higher particle concentrations are ascertained in areas that generate emissions (e.g. continuous urban fabric and port areas) with low SVF values, which lead to constrained dispersion in the urban canopy. In practice, the satellite-derived AOT used in this study cannot capture the fine-scale and local-scale emissions, and the up-scaled figure is more likely what MERIS and AATSR “see”. The results presented next were based on block-kriged values for $1\text{ km} \times 1\text{ km}$ cells surrounding PM stations.

4.2.2. Linear Mixed-Effects Models

Figure 8(a) depicts a scatter-plot of MERIS/AATSR derived AOT values versus 3-D kriged PM_{10} concentrations at $1\text{ km} \times 1\text{ km}$ blocks surrounding each station, during the 2002-2012 time period. It is evident that near surface PM_{10} concentrations are not strongly correlated with total AOT column values ($R = 0.28$). AOT represents columnar aerosol from the surface to the top of the atmosphere, while PM_{10} mass concentration corresponds to suspending particles with diameter less than $10\text{ }\mu\text{m}$ close to the surface. Subsequently, AOT is not representative of PM_{10} measurements, since PM_{10} is not uniformly distributed in the vertical column.

The model building procedure for $LMM1$ resulted in significant random effects, with high standard deviations for intercepts and $DevAOT$ slopes. The likelihood ratio test indicated that the model with day-specific random intercepts was significantly improved relative to the general fixed-effects model, with $L = 16897.897$ ($df = 1$, $p\text{-value} < 0.001$). The AIC and BIC scores were also substantially smaller: 37665.11 and 37713.21, respectively, compared

to 54561.00 and 54602.23. The same conclusions were drawn for the inclusion of day-specific random slopes for *DevAOT*, *DevSTMP*, *DevRHUM* and *DevKIND* with $AIC = 37016.71$ and $BIC = 37161.02$ for the optimal random structure. ML estimation, used for comparison of models with nested fixed effects and the same random structure, resulted in significant (at p -value < 0.001) fixed intercept and fixed *DevSTMP* and *DevRHUM* slopes, leading to the following form:

$$\begin{aligned} \log(PM10[kriged]_{ij}) = & (3.22 + b_{0,j}) + b_{1,j}DevAOT_{ij} + (0.04 + b_{2,j})DevSTMP_{ij} + \\ & + (0.004 + b_{3,j})DevRHUM + b_{4,j}DevKIND_{ij} + \epsilon_{ij} \end{aligned} \quad (17)$$

$$\text{with: } \Psi = \begin{bmatrix} 0.38 & 0.15 & 0.05 & 0.05 & -0.13 \\ 0.15 & 0.29 & 0.18 & 0.27 & 0.16 \\ 0.05 & 0.18 & 0.06 & 0.72 & -0.59 \\ 0.05 & 0.27 & 0.72 & 0.02 & -0.52 \\ -0.13 & 0.16 & -0.59 & -0.52 & 0.03 \end{bmatrix} \quad \text{and } \epsilon_{ij} \sim \mathcal{N}(0, 0.009).$$

It should be noted that the diagonal elements of Ψ report standard deviations and the off-diagonal elements report correlations instead of covariances as correlations are more useful for diagnostic purposes (strongly correlated random effects suggest over-parameterized models).

The (out of sample) predictive performance of *LMM1* (Fig. 8 b) was satisfactory: 5-fold cross-validated $R^2 = 0.95$, with *MAE*, *MAPE* and *MDAPE* considerably small (Table 8 *LMM1* part, 1st column). Moreover, cross-validation results suggest that estimations were unbiased ($ME = 0.12$) which is important when producing estimates to support risk assessment and epidemiological studies. The leave-one-pixel-out cross-validation experiment used to examine whether the model could be generalized to any grid cell in the study domain performed equally well. The 2nd column of Table 8 (*LMM1* part) presents site-specific comparisons between kriged and estimated *PM10* concentrations using *LMM1*. Results suggest that estimations are reliable for the majority of spatial sites.

For *LMM2a*, the model building procedure did not result in significant random effects, with the intercept being the only coefficient displaying significant location-specific deviations. The likelihood ratio test, as well as AIC and BIC values, indicated that site-specific random slopes for satellite-derived products were not significant, leading to unnecessary model complexity. This is supporting the hypothesis stated in Lee et al. (2011): parameters influencing the relationship between *PM* and *AOT* do not display significant spatial variability. AIC and BIC scores suggested that the model with autoregressive residual structure was highly significant, hence it was kept in the optimal random structure. The fitted model is formulated as follows:

$$\begin{aligned} \log \left(PM10[kriged]_{ij} \right) = & (3.28 + b_{0,i}) - 0.05WP + 0.07Mon + 1.24DevAOT_{ij} + \\ & + 0.03DevSTMP_{ij} + 0.002DevRHUM_{ij} - 0.02DevKIND_{ij} - \\ & - 0.22WP : DevAOT_{ij} + 0.03WP : DevTEMP_{ij} + 0.02WP : DevKIND_{ij} + \epsilon_{ij} \end{aligned} \quad (18)$$

where *WP* is a dummy variable that represents the warm season (May to October), *Mon* a dummy variable for Mondays, $b_{0,i} \sim \mathcal{N}(0, 0.004)$, $\epsilon_{i,j} = 0.57 \cdot \epsilon_{i,j-\Delta t} + a_{ij}$ and $a_{ij} \sim \mathcal{N}(0, 0.10)$.

It is interesting to note that the model in Eq.18 contains season-specific effects for all satellite-derived covariates except *DevRHUM*. The first two columns in Table 8 (*LMM2a* part) depict the corresponding values of *ME*, *MAE*, *MAPE* and *MDAPE*, using both cross-validation methods. The outcome is clearly inferior relative to *LMM1*; this result manifests the effect of avoiding daily calibration of satellite-derived products with in situ *PM* concentrations.

The 2-regime analysis resulted in a K-Index threshold equal to $th = 280$, with 43% of the observations below the threshold. *LMM2b* is formulated as

follows:

$$\begin{aligned}
\log \left(PM10[kriged]_{ij} \right) = & (3.25 + b_{0,i}) - 0.05WP + 0.07Mon + 1.24DevAOT_{ij} + \\
& + 0.02DevSTMP_{ij} + 0.005DevRHUM_{ij} - 0.03DevKIND_{ij} - \\
& - 0.19WP : DevAOT_{ij} + 0.01WP : DevSTMP_{ij} + 0.02WP : DevKIND_{ij} + \\
& + 0.04AI : DevAOT_{ij} + 0.01AI : DevKIND_{ij} - 0.003AI : DevRHUM_{ij} + \epsilon_{ij}
\end{aligned} \tag{19}$$

with AI a dummy variable that represents Atmospheric Instability ($KIND > 280$), $b_{0,i} \sim \mathcal{N}(0, 0.004)$, $\epsilon_{i,j} = 0.55 \cdot \epsilon_{i,j-\Delta t} + a_{ij}$ and $a_{ij} \sim \mathcal{N}(0, 0.10)$. *LMM2b* resulted in a small improvement of the performance metrics in the cross-validation experiment, relative to *LMM2a* (Table 8 *LMM2b* part, columns 1-2). Following a suggestion from a referee, to evaluate the importance of satellite-derived covariates we performed a sensitivity analysis based on 5-fold cross-validation to our *LMM2* models, for which accuracy in terms of Mean Absolute Error (MAE) was close to $7.5 \mu g m^{-3}$: MAE increased to 8.14 when *DevAOT* was removed and further increased to 9.47 when all satellite-derived covariates were removed (hence only seasonal dummies remained in the mixed-effects model specifications).

4.3. Estimation of *PM2.5*

4.3.1. Kriging

Due to the small number of in situ *PM2.5* measurements, which resulted in a large number of singular variogram models in the 2-D case, the only interpolation method applied was 3-D kriging. Furthermore, in agreement with the interpolation of *PM10* concentrations, 3-D kriging was applied to residuals of Eq.3. *PM2.5* concentrations were not associated to *LUC* the same way as *PM10*; this most probably relates to different emission sources, e.g. highest *PM2.5* were observed at the stations falling in the “Other roads and associated land” class, as expected, since the main *PM2.5* source is transportation. However, due to the small number of stations, the same categorization derived for *PM10* was used, since pairwise comparisons of average *PM2.5* concentrations didn’t lead to statistically significant results.

Preliminary investigations based on a cross-validation experiment suggested that the spherical variogram was again the best performing model in capturing space-time dependencies of $PM_{2.5}$ concentrations. The estimated parameters ps, n and r , the scales giving best cross-validation results per day and the corresponding performance metrics are presented in Table 7. Figures 7(c) and 7(d) show an example of the kriged surface for the whole study area, before and after up-scaling. As expected, the small number of in situ $PM_{2.5}$ measurements and the fact that daily satellite-derived covariates have not been taken into account at this stage, resulted in a non-representative image for the whole domain. Again, only the kriged values at cells containing PM stations were used in further analyses.

4.3.2. Linear Mixed-Effects Models

Figure 8(c) shows the scatter-plot between available AOT values and kriged $PM_{2.5}$ concentrations at $1\text{ km} \times 1\text{ km}$ blocks surrounding each station during the study period. Again, there was weak correlation ($R = 0.19$) between near surface $PM_{2.5}$ concentrations and columnar AOT values. Once more, a significant improvement was achieved by applying $LMM1$ (Fig.8(d) and 3rd column of Table 8, $LMM1$ part). The estimated model took the following form:

$$\begin{aligned} \log \left(PM_{2.5}[kriged]_{ij} \right) = & (2.65 + b_{0,j}) + b_{1,j}DevAOT_{ij} + b_{2,j}DevSTMP_{ij} \\ & + 0.04WP : DevSTMP_{ij} + b_{4,j}DevKIND_{ij} + \epsilon_{ij} \end{aligned} \quad (20)$$

$$\text{with: } \Psi = \begin{bmatrix} 0.38 & -0.05 & 0.42 & -0.17 \\ -0.05 & 0.35 & -0.51 & -0.65 \\ 0.42 & -0.51 & 0.04 & 0.45 \\ -0.17 & -0.65 & 0.45 & 0.02 \end{bmatrix} \text{ and } \epsilon_{ij} \sim \mathcal{N}(0, 0.02).$$

Notably, Eq.20 suggests stronger effects of temperature in the warm season, which was not observed for PM_{10} in Eq.17. The model displayed satisfactory out of sample performance with $R^2 > 0.85$ for both 5-fold and leave-one-pixel-out cross-validations. MAE , $MAPE$ and $MDAPE$ were larger relative to what

was observed for PM_{10} with accuracy, defined as $1 - MAPE$, close to 90% and
 540 low bias ($ME = 0.25 \mu g m^{-3}$).

In accordance to what was observed in the predictive models for PM_{10} , the model building procedure for $LMM2a$ and $LMM2b$ resulted in significant random intercepts; that is, location-specific variations in the effects of satellite-derived predictors were not statistically significant. $LMM2a$ and $LMM2b$ are formulated as follows:

$$\begin{aligned} \log \left(PM_{2.5}[kriged]_{ij} \right) = & (2.69 + b_{0,j}) + 1.86 DevAOT_{ij} + 0.06 DevSTMP_{ij} - \\ & -0.03 DevKIND_{ij} - 0.97 WP : DevAOT + 0.03 WP : DevKIND \epsilon_{ij} \end{aligned} \quad (21)$$

with $b_{0,i} \sim \mathcal{N}(0, 0.008)$, $\epsilon_{i,j} = 0.58 \cdot \epsilon_{i,j-\Delta t} + a_{ij}$ and $a_{ij} \sim \mathcal{N}(0, 0.13)$.
 and

$$\begin{aligned} \log \left(PM_{2.5}[kriged]_{ij} \right) = & (2.64 + b_{0,j}) + 2.03 DevAOT_{ij} + 0.04 DevSTMP_{ij} - \\ & -0.03 DevKIND_{ij} - 0.70 WP : DevAOT + 0.03 WP : DevKIND - \\ & -0.56 AI : DevAOT_{ij} + 0.02 AI : DevSTMP_{ij} + 0.01 AI : DevKIND_{ij} + \epsilon_{ij} \end{aligned} \quad (22)$$

with $b_{0,i} \sim \mathcal{N}(0, 0.004)$, $\epsilon_{i,j} = 0.55 \cdot \epsilon_{i,j-\Delta t} + a_{ij}$ and $a_{ij} \sim \mathcal{N}(0, 0.10)$.

The predictive performance of $LMM2a$ and $LMM2b$ is inferior relative to $LMM1$ (Table 8, $LMM2a$ and $LMM2b$ parts). Again, a small improvement of the performance metrics in the cross-validation experiment was achieved when
 545 the K-Index was used as a dichotomous estimator of aerosol vertical mixing height. The estimated AOT slopes for the two regimes (high versus low atmospheric instability) are significantly different; this can be attributed to diverse mixing conditions of the aerosols under stable or unstable atmospheric conditions. In contrast to what was observed for PM_{10} , the effects of $DevRHUM$
 550 were not statistically significant in $LMM2a$ and $LMM2b$. 5-fold MAE increased from 5.21 to $6.48 \mu g m^{-3}$ when all satellite derived covariates were removed (5.66 when only AOT was removed).

4.4. Discussion

Previous studies that focused on the estimation of the spatial distribution
 555 of particulate matter concentrations, were mostly performed on large scales,

relying on $10\text{ km} \times 10\text{ km}$ *AOT* from MODIS. Practitioners such as urban planners, as well as epidemiologists are interested in estimating the spatial distribution of daily mean *PM* concentration at finer scales. The results of the cross-validation experiments presented in the previous sections, showed that
560 application of mixed-effects models with day-specific random effects using high resolution ($1\text{ km} \times 1\text{ km}$) satellite-derived products, has the potential to meet their needs.

Regression-kriging (2-D and 3-D) could be used to produce high-resolution daily *PM* maps for the entire study area, based on in-situ *PM* measurements,
565 *LUC* and *SVF* static data, which account for local industrial, domestic and traffic related air pollution. However, in this case, no information from satellite-derived products is used, leading to non-representative maps when a small number of in-situ *PM* measurements is available. The use of *AOT*, *RHUM*, *STMP* and *KIND* allowed better assessment of the spatio-temporal dynamics of *PM*,
570 since these predictors captured differences in particulate matter concentrations among grid cells. Hence, daily calibration of satellite products with block-kriged *PM* in areas close to air-quality stations, can be used to produce urban *PM* maps, which are relevant in studies that associate *PM* to short-term acute effects of air pollution.

The results of mixed-effects models with day-specific random effects are comparable to the ones presented in Nordio et al. (2013) for estimation of *PM*₁₀ and in Kloog et al. (2011) for estimation of *PM*_{2.5} concentrations. Improved out of sample performance metrics can be attributed to the use of block-kriged instead of in situ *PM* concentrations as the variability of spatial averages is reduced relative to the variability of measurements with point-level support. On
580 the other hand, mixed-effects models with site-specific random effects, which can be transferred to areas with no daily in situ data, displayed inferior predictive performance. Application of such models is promising though, in view of the fast evolving satellite remote sensing products. Reassessment of these
585 models using satellite observations with higher temporal resolution and better data quality, is expected to lead to improved performances.

The operational application of *LMM1* for a new day J , requires both in situ and satellite measurements, data homogenization (Sections 4.2.1 and 4.3.1) and re-estimation of Eq.17 and 20 using pixels that correspond to measurement locations, to derive the (day-specific) random effects $b_{0,J}-b_{4,J}$. The updated version
590 of Eq.17 and 20 can be used to produce $PM10[kriged]$ and $PM2.5[kriged]$ for all pixels with available satellite-derived measurements. If, on the other hand, in situ data are not available, one may estimate $PM10[kriged]$ and $PM2.5[kriged]$ based solely on satellite products using directly Eq.19 and 22; random intercepts
595 can be substituted with their expected value which is zero. In such a case one should expect a substantial drop in estimation accuracy as shown in Table 8.

Figure 9(a) shows the spatial pattern of estimated average $PM10$ concentrations derived from the satellite observations for the entire study period (2002-2012), using mixed-effects models with day-specific random effects at
600 $1\text{ km} \times 1\text{ km}$ resolution. Figure 9(b) shows the corresponding map for $PM2.5$. Both maps partition concentrations into ten equally sized bins. Estimated $PM10$ concentrations range from $27.89\text{ }\mu\text{gm}^{-3}$ to $33.35\text{ }\mu\text{gm}^{-3}$, whereas estimated $PM2.5$ values lie between $16.25\text{ }\mu\text{gm}^{-3}$ and $19.72\text{ }\mu\text{gm}^{-3}$. The estimated values are slightly higher than averages observed at the stations (Table
605 4); a plausible explanation is that during the winter time fewer satellite *AOT* products are available, which resulted in increased overall mean *AOT* values and therefore, increased levels of estimated PM concentrations. Remarkably, *LMM1* resulted in lower estimated PM levels for agricultural and green urban areas (Categories I-II in Fig. 4 b) and higher concentrations for industrial, continuous urban fabric and port areas (Categories IV-VI in Fig. 4 b) without the
610 use of these spatial predictors in mixed-effects models; the same was observed for $PM2.5$ despite the small number of in situ measurements. These findings suggest that satellite-derived products are able to capture the spatial variability of PM at $1\text{ km} \times 1\text{ km}$ scale in the areas of investigation.

615 5. Conclusions

Geostatistical investigations that permit inferences relating to potential associations between satellite-based products and ground-based geophysical parameters continues to be an active topic in both research and practice. For meaningful interpretation of the association among these variables based on
620 valid statistical inference, inhomogeneous spatial supports need to be taken into consideration.

This study estimated surface PM_{10} and $PM_{2.5}$ concentrations over the area of Greater London, based on in situ PM measurements and satellite-derived covariates. The latter included AOT from the MERIS/AATSR synergy, as well as
625 $RHUM$, $STMP$ and $KIND$ from MODIS. Moreover, LUC and SVF products were incorporated to account for the local scale emissions, sequestration and diffusion of particles between different monitoring stations. Two kriging methods were applied to in situ PM measurements to take into account different spatial supports of in situ and satellite-derived observations. Predictive models based
630 on the MERIS/AATSR derived AOT on $1\text{ km} \times 1\text{ km}$ produced satisfactory results, with accuracies (defined as $1 - MAPE$ or as $1 - MDAPE$) close to 90% for mixed-effects models with day-specific random effects, for both PM_{10} and $PM_{2.5}$.

The first satellite of the Sentinel 3 series (the Sentinel 3A) is expected to
635 be launched by the European Space Agency (ESA) in late 2015. The synergistic use of the Sea and Land Surface Temperature Radiometer (SLSTR) and the Ocean and Land Color Instrument (OLCI), on board Sentinel-3 satellite (Berger et al., 2012), is expected to provide improved AOT , $RHUM$, $STMP$ and $KIND$ products, and thereby increase the potential to support local scale
640 studies related to urban planning and public health. Furthermore, the simultaneous operation of Sentinel 3A and Sentinel 3B in the near future is expected to provide frequent observations, refining the drawback of relating daily average PM to the MERIS/AATSR synergy AOT , retrieved from a single satellite acquisition. This study may contribute to the development of an operational tool

645 capable of producing high-resolution PM concentration maps using Sentinel-3 series observations. Since all covariates used in the predictive models are satellite-derived products, the methodology can be transferred to other urban areas, to estimate both PM_{10} and $PM_{2.5}$, depending on the availability of in situ measurements to calibrate satellite observations. Additional location-
650 specific covariates can be included in mixed-effects models, in order to explain part of the variability of random effects terms.

While the MERIS and AATSR 11-year data set is suitable for investigating past PM changes and trends in urban areas, the forthcoming SLSTR and OLCI sensors offer the possibility of downscaling, if combined with the high spatial resolution MSI (Multispectral Instrument) onboard Sentinel-2 series (Berger
655 et al., 2012). The common spectral channels of MSI, OLCI and SLSTR provide unique capabilities for synergistic use of observations from these sensors. Such synergistic use is expected to lead to daily PM concentration maps at local scale, which are necessary in urban air quality studies. As a last note,
660 although the analysis described here focused on the estimation of PM_{10} and $PM_{2.5}$ concentrations, the methodology could be easily applied to estimate the spatio-temporal patterns of ultra-fine particles and black carbon, as well as other geophysical quantities such as the turbulent heat exchanges between the urban surface and the atmosphere.

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List of Figure Captions

865 **Figure 1:** (a) The area of Greater London and the geographical distribution of the London Air Quality Monitoring Network PM10 stations. (b) An example of the final AOT distribution product for August 31, 2005.

Figure 2: (a) The Urban Atlas LUC map. (b) SVF for the center of London.

Figure 3: Graphical representation of the developed model: in situ PM data
870 are brought to the spatial scale of the remotely sensed covariates using block-kriging; mixed-effects models are estimated using pixels that contain at least one PM measurement station.

Figure 4: (a) Example of the LUC value assignment to a particular PM location. (b) Merged Raster Map of LUC data at a $100\text{ m} \times 100\text{ m}$ resolution.

875 **Figure 5:** Normal quantile-quantile plot of the regression residuals based on (a) raw PM data and (b) log-transformed data; (c) histogram of the residuals of the second regression model – the red solid curve represents the standard normal distribution.

Figure 6: Seasonal profiles of AOT, STMP, KIND and RHUM. Data from the
880 calibration period (11 years) are shown in grey. Solid curves correspond to NLS estimates and middle dashed curves correspond to NAD. Outer dashed curves estimate the 0.25 and 0.75 quantiles of the AOT, STMP, KIND and RHUM, respectively.

Figure 7: An example of kriged PM10 [μgm^{-3}] surface for September 3, 2011
885 (a) before and (b) after up-scaling. An example of kriged PM2.5 [μgm^{-3}] surface for the same day (c) before and (d) after up-scaling.

Figure 8: Scatter plots of: (a) AOT versus PM10[kriged]; (b) PM10[estimated] by $LMM1$ model versus PM10[kriged]; (c) AOT versus PM2.5[kriged]; (d) PM2.5[estimated] by $LMM1$ model versus PM2.5[kriged]

890 **Figure 9:** Mean concentration [$\mu g m^{-3}$] of **(a)** PM10 and **(b)** PM2.5 in each
1 $km \times 1 km$ grid cell estimated by the *LMM1* mixed-effects models, for
the entire study period (2002-2012).

Table 1: Mean PM10 concentrations for different land cover class.

S.L. – Sealing Layer

#	LUC class	Estimate [μgm^{-3}]	Std.Error [μgm^{-3}]
1	Agricultural - Semi-natural areas - Wetlands	21.01	0.23
2	Sports and leisure facilities	22.25	0.17
3	Green urban areas	23.00	0.17
4	Airports	26.31	0.27
5	Discontinuous Medium D. Urban Fabric (S.L. : 30% - 50%)	26.88	0.05
6	Discontinuous Dense Urban Fabric (S.L. : 50% - 80%)	26.96	0.12
7	Industrial, commercial, public, military and private units	27.38	0.05
8	Port areas	28.09	0.58
9	Other roads and associated land	28.48	0.17
10	Continuous Urban Fabric (S.L. : 50% - 80%)	29.74	0.12

Table 2: p-values for testing the null hypothesis: $\mathbf{H_0 : LUC_i - LUC_j = 0}$ vs $\mathbf{H_1 : LUC_i - LUC_j \neq 0}$.

i \ j	1	2	3	4	5	6	7	8	9
1	-	-	-	-	-	-	-	-	-
2	< 0.001	-	-	-	-	-	-	-	-
3	< 0.001	0.051	-	-	-	-	-	-	-
4	< 0.001	< 0.001	< 0.001	-	-	-	-	-	-
5	< 0.001	< 0.001	< 0.001	0.358	-	-	-	-	-
6	< 0.001	< 0.001	< 0.001	0.443	0.999	-	-	-	-
7	< 0.001	< 0.001	< 0.001	< 0.01	0.022	< 0.001	-	-	-
8	< 0.001	< 0.001	< 0.001	0.107	0.597	0.474	0.957	-	-
9	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.999	-
10	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.108	< 0.001

Table 3: Merged land cover categories.

Category	Land Cover Class
I	Agricultural - Semi-natural areas - Wetlands Forests Land without current use Water bodies
II	Sports and leisure facilities Discontinuous Very Low Density Urban Fabric (S.L. < 10%) Discontinuous Low Density Urban Fabric (S.L. : 10% - 30%) Green urban areas
III	Airports Discontinuous Medium Density Urban Fabric (S.L. : 30% - 50%) Discontinuous Dense Urban Fabric (S.L. : 50% - 80%)
IV	Construction sites Industrial, commercial, public, military and private units Isolated Structures Mineral extraction and dump sites
V	Fast transit roads and associated land Other roads and associated land Port areas Railways and associated land
VI	Continuous Urban Fabric (S.L. > 80%)

Table 4: Annual averages of PM_{10} and $PM_{2.5}$ concentrations from 2002 to 2012. **SE** – Standard Error

Year	# PM_{10} stations	Mean [μgm^{-3}]	SE [μgm^{-3}]	# $PM_{2.5}$ stations	Mean [μgm^{-3}]	SE [μgm^{-3}]
2002	52	28.70	0.09	4	13.59	0.18
2003	54	32.04	0.11	4	16.17	0.22
2004	67	27.45	0.09	4	14.79	0.16
2005	71	28.32	0.10	7	15.39	0.18
2006	77	27.91	0.10	7	16.16	0.15
2007	72	27.41	0.10	12	16.18	0.15
2008	74	25.40	0.08	15	14.96	0.12
2009	72	25.07	0.08	19	14.41	0.09
2010	70	24.91	0.07	18	14.66	0.09
2011	64	26.71	0.09	20	15.62	0.12
2012	54	25.29	0.09	20	14.08	0.11
Overall	-	27.20	0.09	-	15.09	0.14

Table 5: Leave-one-station-out cross validation results of ordinary 2-D kriging using daily variograms (**RMSE** [μgm^{-3}], **ME** [μgm^{-3}], **MAE** [μgm^{-3}] and **R**) applied to raw PM10, log-transformed PM10, residuals of raw PM10 and residuals of log-transformed PM10.

	raw PM10				log PM10			
Year	RMSE	ME	MAE	R	RMSE	ME	MAE	R
2002	8.20	-0.03	5.24	0.77	8.08	-0.14	5.20	0.77
2003	8.58	-0.03	5.85	0.85	8.46	-0.13	5.79	0.85
2004	9.55	-0.04	5.40	0.75	9.36	-0.10	5.31	0.76
2005	10.71	-0.04	6.05	0.74	10.62	-0.06	6.01	0.74
2006	10.84	-0.04	5.91	0.73	10.78	0.03	5.82	0.73
2007	11.03	-0.02	6.29	0.76	10.73	0.07	6.10	0.78
2008	9.28	-0.03	5.86	0.77	9.10	-0.02	5.73	0.78
2009	8.96	-0.02	5.55	0.70	8.69	-0.13	5.48	0.72
2010	8.04	-0.01	5.37	0.71	7.99	-0.14	5.37	0.71
2011	7.61	-0.02	5.47	0.85	7.54	-0.05	5.42	0.85
2012	8.00	-0.07	5.50	0.82	7.87	-0.11	5.44	0.83
Mean	9.16	-0.03	5.66	0.77	9.02	-0.07	5.61	0.78
	Residuals raw PM10				Residuals log PM10			
Year	RMSE	ME	MAE	R	RMSE	ME	MAE	R
2002	7.92	-0.02	5.09	0.78	7.91	-0.21	5.07	0.79
2003	8.17	-0.02	5.49	0.86	8.05	-0.14	5.35	0.87
2004	9.33	-0.03	5.23	0.76	9.19	-0.13	5.14	0.77
2005	10.65	-0.04	5.91	0.74	10.59	-0.16	5.89	0.75
2006	10.80	-0.04	5.79	0.73	10.78	-0.06	5.73	0.73
2007	10.64	-0.01	5.97	0.78	10.44	0.08	5.87	0.79
2008	8.86	-0.03	5.53	0.79	8.79	0.00	5.43	0.80
2009	8.69	-0.02	5.34	0.72	8.44	-0.13	5.27	0.74
2010	7.75	-0.02	5.18	0.73	7.70	-0.14	5.13	0.74
2011	7.22	-0.02	5.14	0.87	7.22	-0.08	5.11	0.87
2012	7.69	-0.05	5.22	0.83	7.55	-0.14	5.10	0.84
Mean	8.88	-0.03	5.44	0.78	8.79	-0.10	5.37	0.79

Table 6: Cross validation results for the interpolation of PM10: 3-D kriging.

Year	n	ps	r [km]	Scale [km/day]	RMSE [μgm^{-3}]	ME [μgm^{-3}]	MAE [μgm^{-3}]	R
2002	0.04	0.11	70	18.0	8.07	-0.08	5.16	0.78
2003	0.03	0.15	90	18.0	8.34	-0.09	5.59	0.86
2004	0.05	0.14	76	14.0	9.48	-0.06	5.42	0.75
2005	0.07	0.17	82	13.5	10.8	-0.10	6.17	0.74
2006	0.07	0.15	84	13.0	10.90	-0.02	5.93	0.73
2007	0.07	0.15	83	16.0	10.44	0.00	5.92	0.79
2008	0.07	0.16	83	14.5	8.91	0.00	5.54	0.79
2009	0.06	0.11	60	14.0	8.57	0.04	5.33	0.73
2010	0.07	0.10	71	17.5	7.87	0.00	5.23	0.73
2011	0.06	0.12	66	11.5	7.55	-0.09	5.41	0.85
2012	0.07	0.13	65	13.5	8.08	-0.12	5.52	0.82
Mean	-	-	-	-	9.00	-0.04	5.58	0.78

Table 7: Cross validation results for the interpolation of PM2.5: 3-D kriging.

Year	n	ps	r [km]	Scale [km/day]	RMSE [μgm^{-3}]	ME [μgm^{-3}]	MAE [μgm^{-3}]	R
2002	0.02	0.15	72	19.0	3.24	-0.01	2.46	0.87
2003	0.00	0.20	62	16.0	3.62	0.15	2.52	0.91
2004	0.01	0.14	50	14.5	4.61	-0.19	3.49	0.75
2005	0.01	0.17	66	19.5	5.42	-0.28	3.49	0.76
2006	0.00	0.20	60	15.5	4.85	0.01	2.87	0.84
2007	0.05	0.16	71	17.5	5.37	-0.06	3.66	0.84
2008	0.07	0.17	61	13.0	5.30	-0.15	3.86	0.79
2009	0.06	0.15	52	11.5	5.04	-0.02	3.54	0.76
2010	0.06	0.14	52	13.0	5.16	0.00	3.82	0.77
2011	0.06	0.17	70	13.0	5.62	-0.02	3.72	0.83
2012	0.08	0.19	65	13.0	5.34	-0.02	3.72	0.82
Mean	-	-	-	-	4.87	-0.05	3.38	0.81

Table 8: Predictive performance of three mixed-effects model specifications.

		PM10		PM2.5	
	Validation Method	5-fold	leave-one-out	5-fold	leave-one-out
<i>LMM1</i>	ME [$\mu g m^{-3}$]	0.12	0.18	0.25	0.47
	MAE [$\mu g m^{-3}$]	2.14	2.06	2.24	2.19
	1- MAPE [%]	92.52	92.89	90.36	88.28
	1- MDAPE [%]	94.15	93.93	87.79	89.83
	Out of sample R²	0.95	0.96	0.86	0.92
<i>LMM2a</i>	ME [$\mu g m^{-3}$]	1.62	1.71	1.40	1.47
	MAE [$\mu g m^{-3}$]	7.62	7.72	5.23	5.34
	1- MAPE [%]	73.28	72.99	69.88	69.78
	1- MDAPE [%]	78.71	78.53	76.12	75.81
	Out of sample R²	0.36	0.37	0.30	0.37
<i>LMM2b</i>	ME [$\mu g m^{-3}$]	1.56	1.64	1.32	1.47
	MAE [$\mu g m^{-3}$]	7.49	7.59	5.21	5.31
	1- MAPE [%]	73.75	73.43	70.04	70.08
	1- MDAPE [%]	79.61	79.22	76.99	76.45
	Out of sample R²	0.38	0.39	0.30	0.37

Figure 1: (a) The area of Greater London and the geographical distribution of the London Air Quality Monitoring Network PM₁₀ stations. (b) An example of the final AOT distribution product for August 31, 2005.

Figure 2: (a) The Urban Atlas LUC map. (b) SVF for the center of London.

Figure 3: Graphical representation of the developed model: in situ *PM* data are brought to the spatial scale of the remotely sensed covariates using block-kriging; mixed-effects models are estimated using pixels that contain at least one *PM* measurement station.

Figure 4: (a) Example of the LUC value assignment to a particular PM location. (b) Merged Raster Map of LUC data at a $100\text{ m} \times 100\text{ m}$ resolution.

Figure 5: Normal quantile-quantile plot of the regression residuals based on (a) raw *PM* data and (b) log-transformed data; (c) histogram of the residuals of the second regression model – the red solid curve represents the standard normal distribution.

Figure 6: Seasonal profiles of AOT, STMP, KIND and RHUM. Data from the calibration period (11 years) are shown in grey. Solid curves correspond to NLS estimates and middle dashed curves correspond to NAD. Outer dashed curves estimate the 0.25 and 0.75 quantiles of the AOT, STMP, KIND and RHUM, respectively.

Figure 7: An example of kriged PM10 [$\mu g m^{-3}$] surface for September 3, 2011 (a) before and (b) after up-scaling. An example of kriged PM2.5 [$\mu g m^{-3}$] surface for the same day (c) before and (d) after up-scaling.

Figure 8: Scatter plots of: (a) AOT versus PM10[kriged]; (b) PM10[estimated] by *LMM1* model versus PM10[kriged]; (c) AOT versus PM2.5[kriged]; (d) PM2.5[estimated] by *LMM1* model versus PM2.5[kriged]

Figure 9: Mean concentration [μgm^{-3}] of (a) PM10 and (b) PM2.5 in each $1\text{ km} \times 1\text{ km}$ grid cell estimated by the *LMM1* mixed-effects models, for the entire study period (2002-2012).