Atmospheric Environment 95 (2014) 82–88

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

New functions for estimating AOT40 from ozone passive sampling

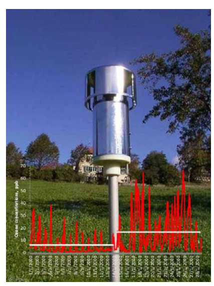
Alessandra De Marco [a,*], Marcello Vitale [b], Umit Kilic [c], Yusuf Serengil [c], Elena Paoletti [d]

[a] Italian National Agency for New Technologies, Energy and The Environment (ENEA), C.R. Casaccia, Via Anguillarese 301, 00123 S. Maria di Galeria, Rome, Italy
[b] Department of Environmental Biology, "Sapienza" University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy
[c] University of Istanbul, Faculty of Forestry, Department of Watershed Management, Bahcekoy-Sarıyer, Istanbul, Turkey
[d] IPSP-CNR, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy

HIGHLIGHTS

- The Loibl function is inadequate to accurately predict AOT40 in Italy.
- New statistical models were built for estimating AOT40 from passive sampling.
- Multi-variate, non-linear regression models work better than Loibl approach in estimating AOT40.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 January 2014
Received in revised form
5 June 2014
Accepted 9 June 2014
Available online 10 June 2014

Keywords:
Tropospheric ozone
Passive sampling
AOT40
Loibl function
Ozone monitoring

ABSTRACT

AOT40 is the present European standard to assess whether ozone (O_3) pollution is a risk for vegetation, and is calculated by using hourly O_3 concentrations from automatic devices, i.e. by active monitoring. Passive O_3 monitoring is widespread in remote environments. The Loibl function estimates the mean daily O_3 profile and thus hourly O_3 concentrations, and has been proposed to calculate AOT40 from passive samplers. We investigated whether this function performs well in inhomogeneous terrains such as over the Italian country. Data from 75 active monitoring stations (28 rural and 47 suburban) were analysed over two years. AOT40 was calculated from hourly O_3 data either measured by active measurements or estimated by the Loibl function applied to biweekly averages of active-measurement hourly data. The latter approach simulated the data obtained from passive monitoring, as two weeks is the usual exposure window of passive samplers. Residuals between AOT40 estimated by applying the Loibl function and AOT40 calculated from active monitoring ranged from +241% to −107%, suggesting that the Loibl function is inadequate to accurately predict AOT40 in Italy. New statistical models were built for both rural and suburban areas by using non-linear models and including predictors that can be easily measured at forest sites. The modelled AOT40 values strongly depended on physical predictors (latitude and longitude), alone or in combination with other predictors, such as seasonal cumulated ozone and elevation. These results suggest that multi-variate, non-linear regression models work better than the Loibl-based approach in estimating AOT40.

1. Introduction

Ozone (O_3) is a natural component of the atmosphere. The majority of tropospheric O_3 formation occurs when O_3 precursors such as nitrogen oxides (NOx), carbon monoxide (CO) and volatile

* Corresponding author.
E-mail address: alessandra.demarco@enea.it (A. De Marco).

http://dx.doi.org/10.1016/j.atmosenv.2014.06.021

organic compounds (VOCs), react in the atmosphere in the presence of sunlight. Motor vehicle exhaustions, industrial emissions, and chemical solvents are the major anthropogenic sources of these chemicals. Although they often originate in urban areas, winds transport precursors hundreds of kilometres, causing O_3 formation in sparsely populated regions as well. Even though emission of O_3 precursors have decreased since the '90s (−2.3% per year NO*x*, −3.0% per year Non-Methane VOC), background O_3 concentrations are globally increasing (Zhang et al., 2008; Sicard et al., 2013; Paoletti et al., 2014).

Ozone is a short-lived climate pollutant and is strongly influenced by many geographical parameters. A number of studies have found a relationship between O_3 and altitude, such that sites at higher altitude experience higher O_3 compared to sites at lower altitude (Gibson et al., 2009; Ribas and Peñuelas, 2006; Sanz et al., 2007). Other important factors for explaining O_3 variations at local scale are: the proximity to the cities, as they are significant NOx sources (Sundberg et al., 2006), and the distance from the coastline, that can be associated with an increase of O_3 concentration in coastal areas (Papanastasiou and Melas, 2009).

Ozone negatively affects plants in several ways, in particular by setting up a variety of defensive strategies (Di Baccio et al., 2008), reducing stomatal conductance and the control on water loss (Hoshika et al., 2012), and reducing the uptake of atmospheric carbon by vegetation (Fares et al., 2013). Stomata largely control O_3 uptake. Even if stomatal O_3 uptake is becoming important for risk assessment (Paoletti and Manning, 2007), at the moment the legislative standard used in Europe for the protection of vegetation is AOT40, which is based on exposure only. AOT40 is defined as the sum of hourly O_3 concentrations exceeding the threshold of 40 ppb over the growing season (for forests from April 1st to September 30th) in the daylight time (UNECE, 2010). Thus, hourly O_3 data are needed to calculate AOT40, but they are often unavailable at remote sites. Active monitoring provides hourly O_3 concentrations but requires power, which usually prevents sampling in rural areas and forests (Cox, 2003). Passive sampling is widely used in rural areas for its low cost and requirements (Krupa and Legge, 2000; Cox and Malcom, 1999), but the data are obtained in form of average over the time window of exposure, usually two weeks. Passive sampling gives a cumulated O_3 value only, and does not account for the large temporal variations of hourly O_3 concentrations in a day. Significant uncertainties have been attributed to passive sampling (Krupa and Legge, 2000) and must be evaluated in the context of an important property of the AOT40 index, namely its high sensitivity to concentration changes (Tuovinen, 2000). There were several attempts to estimate hourly values and cumulative indices such as AOT40 from O_3 passive samplers (Krupa et al., 2001, 2003; Tuovinen, 2002; Krupa and Nosal, 2001).

A method for estimating AOT40 from passive sampling was developed by Mazzali et al. (2002) who used the Loibl function (Loibl et al., 1994, 2004). This function describes the mean daily O_3 profile in a site as a function of relative altitude (difference between the altitude of the site and the lowest altitude within a 5 km radius). Although serious deviations occurred at individual sites, the feasibility of this approach was confirmed by comparing co-located passive and active samplers at 20 forest sites in France, Italy, Spain and Switzerland over the period 2000–2002 and by simulating passive sampling by weekly O_3 averages obtained from active monitoring at 17 sites in Italy (Gerosa et al., 2007). A small-scale application in an Italian region (Trentino) also suggested that the Loibl function worked well in simulating daily profiles of O_3 and thus calculating AOT40, although in a few cases the differences between the AOT40 estimates were very high, i.e. 80–120% (Gottardini et al., 2010). The approach by Gerosa et al. (2007) is mentioned in the ICP-Forests manual as a methodology for estimating hourly O_3 concentrations from passive samplers (Schaub et al., 2010). ICP-Forests is the world's largest monitoring network, providing data on forest health, air pollution, climate change and biodiversity in European forests. Hourly O_3 concentrations obtained from passive monitoring were also used to calculate stomatal O_3 fluxes of forests (Schaub et al., 2007). There is a general consensus about stomatal O_3 flux, i.e. the instantaneous rate at which O_3 is absorbed via stomata, leading to a biologically more relevant estimate of O_3 risk as compared to exposure indices such as AOT40 (Matyssek et al., 2007). There is thus a need to corroborate the use of the Loibl function in deriving hourly O_3 concentrations for estimating AOT40 and eventually stomatal O_3 flux.

To this aim, the performance of the Loibl function in estimating AOT40 was analysed at 75 Italian monitoring sites distributed all over the Italian peninsula and representative of an inhomogeneous terrain. In order to develop new statistical functions for estimating AOT40, multi-variate, non-linear models were applied to both suburban and rural sites.

2. Materials and methods

2.1. Data collection

Seventy-five rural and suburban O_3 monitoring stations with a >75% growing season coverage of hourly O_3 data were selected from the BRACE database (BRACE, 2006) and from local public institutions (Regional Agencies for Environmental Protection, ARPA) for the time period 2005–2006 (Fig. 1, Table 1S). The type classification of the stations is defined according to the European Air quality database methodology (EUROAIRNET, 1999).

Latitude (Lat), longitude (Long), distance from the closest city ($Urban_{dist}$), and distance from the sea (Sea_{dist}), were calculated by

Fig. 1. Ozone monitoring stations included in the analysis of AOT40.

using the Geographic Information System (Arc GIS 8.1, Esri, Redlands – CA, USA). A Digital Elevation Model (DEM) at 20-m resolution was used to derive altitude and minimum and maximum elevation within a 5 km radius ($MIN_{\_5km}$ and $MAX_{\_5km}$, respectively). Meteorological data from 72 stations of the Research unit for Climatology and Meteorology applied to Agriculture (CMA, 2006) were used for calculating maximum (T_{max}) and minimum temperature (T_{min}) during the growing season. Because the meteorological stations were not co-located with the ozone measuring stations, kriging analysis was performed to interpolate the data, according to the methodology by De Marco et al. (2010). Kriging is a geo-statistical interpolation technique considering both the distance and the degree of variation between known data points, for estimating values in areas with no monitoring stations. A kriging estimate is a weighted linear combination of the known sample values around the point to be analysed. Kriging allows deriving weights, which result in optimal and unbiased estimates. In this work, kriging technique was based on ordinary kriging.

2.2. AOT40 estimation

Biweekly O_3 concentrations (biweeklyO_3) were calculated from active measurements of hourly concentrations and used for deriving hourly O_3 concentrations (weightedO_3) by applying the Loibl function as follows:

$$O_3(h_r,t)=\left(a_1+a_2e^{-(t-a_3)^2a_4}\right)\ln\left(\frac{h_r}{100}+\frac{b_1t^2+b_2t+b_3}{b_4t^2+b_5t+10{,}000}e^{-b_6t}\right) \quad (1)$$

Where h_r is the relative altitude given by the difference between the absolute altitude and that of the point located in the lowest position within a radius of 5 km, t is the time of the day, a_1, a_2, a_3, a_4 and b_1, b_2, b_3, b_4, b_5, b_6 are the coefficients obtained by Loibl et al. (1994) for Austrian sites. According to the methodology described in Gerosa et al. (2003), the hourly Loibl-estimated O_3 concentrations were then weighted on the basis of biweekly O_3 concentrations, as obtained from passive sampling measurements:

$$\mathrm{weightedO_3} = (\mathrm{biweeklyO_3}/\mathrm{dailyO_3}(\mathrm{hr,t}))*\mathrm{O_3}(\mathrm{hr,t}) \quad (2)$$

where O_3(hr,t) is the hourly O_3 concentration estimated by the Loibl function, dailyO_3(hr,t) is the daily average of O_3(hr,t).

AOT40 was calculated from measured hourly O_3 data ($AOT40_{meas}$) and from Loibl-derived O_3 concentrations ($AOT40_{est}$) according to the usual Formula (3):

$$\mathrm{AOT40} = \sum \max((\mathrm{C}-40),0)\mathrm{d}t \quad (3)$$

where C is hourly ozone concentration (ppb) and dt is 1 h. The summation is over all hourly values measured between 8:00–20:00 Central European Time each day in the 6-month growing season from 1 April to 30 September (UNECE, 2010).

2.3. AOT40 modelling and data analysis

General Regression Model (GRM) applies the methods of the general linear model, allowing to build models for designs with multiple-degrees-of-freedom effects for categorical predictor variables, as well as for designs with single-degree-of-freedom effects for continuous predictor variables. The GRM approach used here implements stepwise and best-subset model-building techniques for Analysis of Variance (ANOVA), regression and analysis of covariance (ANCOVA) designs. To build models and to estimate and test hypotheses about effects included in the final model, the least squares method of the general linear model was applied. In this paper the application of GRM to generate statistical models was based on the Response Surface Regression. The quadratic response surface regression designs were a hybrid type of design with characteristics of both polynomial regression designs and fractional factorial regression designs. Quadratic response surface regression designs contained all the same effects of polynomial regression designs to degree 2 and additionally the 2-way interaction effects of the predictor variables (Myers and Montgomery, 1995). Software used for statistical analysis was Statistica 8.0 (StatSoft inc, Tulsa, OK – USA).

The regression equation for a quadratic response surface regression design for three continuous predictor variables P, Q, and R would be (Equation (4)):

$$Y = k_0 + k_1P + k_2P^2 + k_3Q + k_4Q^2 + k_5R + k_6R^2 + k_7P \times Q + k_8P \times R + k_9Q \times R \quad (4)$$

AOT40 was considered as dependent variable, whereas the predictors were: latitude (Lat), longitude (Long), maximum and minimum temperature (T_{max} and T_{min}, respectively), cumulated ozone (O_3cum) and averaged ozone (O_3) on the overall time frame (growing season), distance from the closest city (Urban_Dist), distance from the sea (Sea_Dist) and minimum, maximum elevation within a 5 km radius ($MIN_{\_5km}$ and $MAX_{\_5km}$, respectively). Cumulated ozone (O_3cum) was calculated as the sum of the biweekly O_3 averages, and integrates exposure level (O_3 average) and exposure window (length of the growing season). The biweekly values correspond to the values obtained from passive sampling.

Cross-validation refers to the process of assessing the predictive accuracy of a model in a test sample (sometimes also called a cross-validation sample) relative to its predictive accuracy in the learning sample from which the model was developed. A proportion of the cases (70% of the dataset) was arbitrarily designated as belonging to the learning sample and the remaining cases were designated as belonging to the test sample (30% of the dataset). A stratified random sampling was performed to select the 30% in each year and station type.

The GRM model was developed by using the cases in the learning sample, and its predictive accuracy was assessed by using the cases in the test sample (cross-validation).

Residuals between $AOT40_{meas}$ and $AOT40_{est}$ and between $AOT40_{meas}$ and AOT40 modelled by GRM were calculated as percentage of the latter minus the former divided by the former.

3. Results

Individual sites showed marked differences in the residuals between $AOT40_{meas}$ (with hourly values from active monitoring) and $AOT40_{est}$ (with hourly values from the Loibl approach) at suburban (Fig. 2A) and rural stations (Fig. 2B). In two cases, the differences were very high reaching a percentage of variation of 241% (2005) and 203% (2006). In 40% of cases, the Loibl-based $AOT40_{est}$ underestimated $AOT40_{meas}$, i.e. the residuals were below the red lines of null variation in Fig. 2. Such an underestimation ranged from −80% to −3% (−37% on average) and from −107% to −4% (−31% on average) for rural and suburban stations, respectively. $AOT40_{est}$ overestimated $AOT40_{meas}$ in 50% and 60% of the rural and suburban stations, respectively. The range of overestimation was from 5% to 203% (51% on average) and from 4% to 241% (53% on average) for rural and suburban stations, respectively.

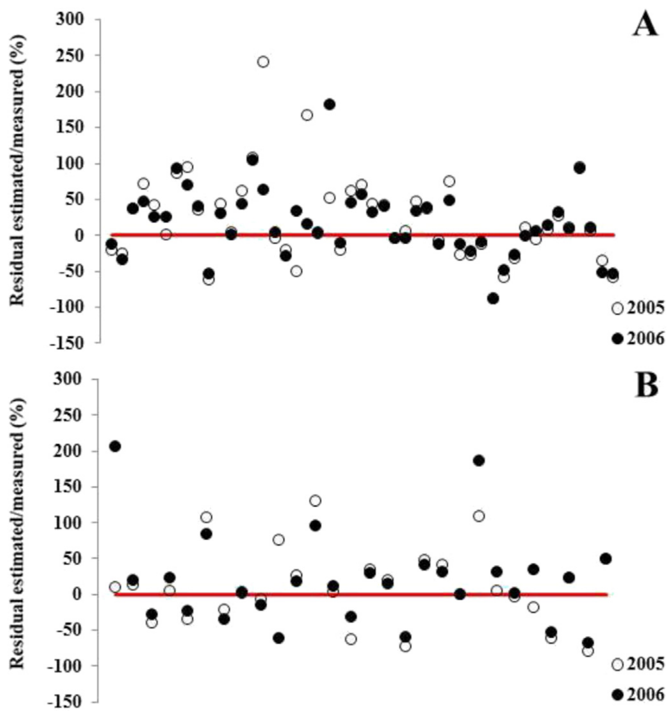


Fig. 2. Residuals (%) between AOT40 values estimated by applying the Loibl function to biweekly averages of hourly measurements ($AOT40_{est}$) and AOT40 values calculated from hourly measurements ($AOT40_{meas}$) at suburban (A) and rural (B) stations. Empty dots are for the year 2005 and full dots are for the year 2006. The *x*-axis represents the monitoring stations. A red line shows null percentage variation.

Table 1
Parameter estimates based on the GRM analysis for rural and suburban stations. Significant predictors are: longitude (Long), latitude (Lat), elevation, minimum elevation around a 5 km buffer (MIN_5 km), maximum elevation around a 5 km buffer (MAX_5 km), distance from the closest city (Urban_Dist), distance from the sea (Sea_Dist), Ozone (O_3, annual average), Cumulated Ozone (O_3cum, i.e. the summation of the biweekly values obtained from passive sampling over the growing season). Only significant parameters, singly and/or linear – non-linear combinations, are shown.

Both station types	Param.	Std.Err.	*t*	*P*
Intercept	−1.51E+04	3.81E+03	−3.968	<0.001
Long*elevation	−1.35E-05	6.09E-06	−2.218	0.028
Long*MIN_5 km	5.21E-05	1.07E-05	4.894	<0.001
Long*MAX_5 km	−8.01E-06	2.32E-06	−3.462	<0.001
elevation*Urban_Dist	−3.13E-04	1.27E-04	−2.464	0.015
Lat* O_3cum	1.20E-06	1.10E-07	10.886	<0.001
$AOT40_{total}$	*Multiple R*	*Multiple R^2*	*Adjusted R^2*	*SS*
	0.812	*0.659*	*0.641*	*9.151E+09*
Suburban				
Intercept	−8.29E+03	6.20E+03	−1.338	0.186
Long*MAX_5 km	−4.38E-06	1.78E-06	−2.463	0.016
Long*Tmin	−6.39E-04	2.52E-04	−2.540	0.013
Lat* O_3cum	1.15E-06	1.60E-07	7.151	<0.001
$AOT40_{suburban}$	*Multiple R*	*Multiple R^2*	*Adjusted R^2*	*SS*
	0.754148	*0.568740*	*0.545217*	*3.310E+09*
Rural				
Intercept	1.61E+02	2.88E+03	0.056	0.955
MIN_5 km	3.39E+01	8.51E+00	3.978	<0.001
Long*Sea_Dist	1.13E-07	4.14E-08	2.715	0.010
elevation*Urban_Dist	−5.29E-04	1.51E-04	−3.504	0.001
MAX_5 km* O_3cum	−1.14E-03	3.49E-04	−3.272	0.002
O_3*O_3cum	7.82E-02	1.01E-02	7.710	<0.001
$AOT40_{rural}$	*Multiple R*	*Multiple R^2*	*Adjusted R^2*	*SS*
	0.893	*0.798*	*0.770*	*5.969E+09*

GRM highlighted a statistically significant dependence of $AOT40_{total}$ – i.e. the AOT40 calculated for both suburban and rural sites - from linear combinations of: O_3cum with latitude; longitude with elevation, minimum and maximum elevation around a 5 km buffer; and elevation with urban distance (Table 1). The overall model showed a multiple determination coefficient of 0.66. When the dataset was subdivided in suburban and rural stations, GRM showed different dependences of AOT40 from the predictors. AOT40 at suburban sites ($AOT40_{suburban}$) was significantly affected by a combination of: longitude and maximum elevation around a 5 km buffer or minimum temperature; and latitude with O_3cum (Table 1). The most significant predictors for AOT40 at rural sites ($AOT40_{rural}$) were minimum elevation around a 5 km buffer, altitude combined with urban distance, cumulated ozone combined with maximum elevation around a 5 km buffer or annual ozone average, and longitude combined with distance from the sea. The multiple determination coefficients were 0.57 and 0.67 for the suburban and rural datasets, respectively.

Three new functions were elaborated by the statistical modelling performed on the datasets, i.e. total, suburban and rural monitoring stations. All functions were based on significant predictors (Equations (5)–(7))

$$\begin{aligned}AOT40_{total} = & -1.512\times 104 - \left(1.350\times 10^{-5}\text{Long}\times\text{Elev}\right)\\ & + \left(5.211\times 10^{-5}\text{Long}\times\text{MIN\_5}_{km}\right)\\ & - \left(8.014\times 10^{-6}\text{Long}\times\text{MAX\_5}_{km}\right)\\ & - \left(3.126\times 10^{-4}\text{Elev}\times\text{Urban\_Dist}\right)\\ & + \left(1.200\times 10^{-6}\text{Lat}\times O_3\text{cum}\right)\end{aligned} \quad (5)$$

$$\begin{aligned}AOT40_{suburban} = & -8.289\times 103 - \left(4.380\times 10^{-6}\text{Long}\right.\\ & \left.\times\,\text{MAX\_5}_{km}\right) - \left(6.388\times 10^{-4}\text{Long}\times T_{min}\right)\\ & + \left(1.147\times 10^{-6}\text{Lat}\times O_3\text{cum}\right)\end{aligned} \quad (6)$$

$$\begin{aligned}AOT40_{rural} = & 1.611\times 102 + (3.385\times\text{MIN\_5km})\\ & + \left(1.125\times 10^{-7}\text{Long}\times\text{Sea\_Dist}\right)\\ & - \left(5.288\times 10^{-4}\text{Elev}\times\text{Urban\_Dist}\right)\\ & - \left(1.143\times 10^{-3}O_3\text{cum}\times\text{MAX\_5km}\right)\\ & + \left(7.822\times 10^{-2}O_3\times O_3\text{cum}\right)\end{aligned} \quad (7)$$

The relationships between observed (i.e. calculated from active monitoring hourly data) and predicted AOT40 values (i.e. modelled by Equations (4)–(6)) in the 30% of dataset (cross-validation) are shown in Fig. 3. The high slope values (0.89, 0.88 and 0.92, for Fig. 3A–C, respectively) suggest that these new functions predicted the $AOT40_{meas}$ values very well.

Equations (5)–(7) and Table 1 highlight the role of geographical coordinates, i.e. longitude (Long) and latitude (Lat), in affecting AOT40, even if in combination with other predictors, such as elevation and cumulated ozone. In general, one of the most important predictors for both rural and suburban sites was O_3cum, followed by other predictors which were often in combination (maximum elevation in a 5 km buffer, longitude and latitude). Sea distance and urban distance were important predictors at rural areas, when combined with longitude and altitude, respectively. When GRM models were applied to the validation dataset (30% of

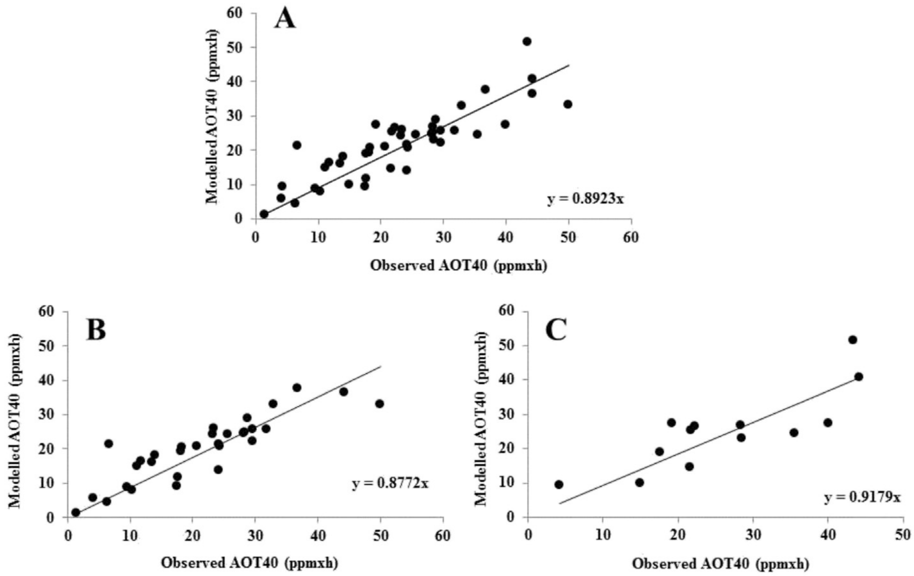


Fig. 3. Cross-validation of the GRM analysis. Relationship between AOT40 predicted by the new functions and observed, i.e. calculated from active monitoring hourly data in total (A), suburban (B) and rural (C) stations for the 30% of data not included in the GRM models.

total dataset) at suburban and rural stations, $AOT40_{meas}$ was underestimated by −6.4% on average, overestimated by 4.1%, and underestimated by −3.2% at suburban, rural and total stations, respectively (Fig. 4A and B).

4. Discussion

A proper estimation of O_3 concentrations and AOT40 at remote sites is critical, as those areas are representative of regional O_3 levels and relevant for O_3 impacts on vegetation. Passive sampling offers considerable practical advantages in O_3 detection in remote areas (Krupa and Legge, 2000), being inexpensive and easy to deploy in the field (Cox and Malcom, 1999). The Loibl function was empirically developed for the Austrian mountainous terrain from a dataset of 9 summer days by assuming that O_3 concentrations depend only on relative altitude (above valley ground) and time of the day (Loibl et al., 1994). This function – with the parameterisation used in the present paper – was applied for estimating AOT40 from passive sampling in an Alpine valley (Mazzali et al., 2002), at forest sites in France, Italy, Spain and Switzerland (Gerosa et al., 2007) and in an Italian region (Gottardini et al., 2010). When compared to AOT40 values from co-located active monitors, however, considerable deviations occurred (Mazzali et al., 2002; Gottardini et al., 2010; Gerosa et al., 2012). Our results do not corroborate the use of this function for estimating AOT40 at monitoring stations distributed all over the Italian territory which is characterised by variable climatic and orographic conditions. Residuals between AOT40 estimated by the Loibl function and AOT40 calculated from active monitoring ranged from +241% to −107% (Fig. 2), suggesting that the Loibl function is inadequate to accurately predict AOT40 from biweekly passive monitoring data in Italy, when the fitting developed by Loibl et al. (1994) and applied in Mazzali et al. (2002), Gerosa et al. (2007, 2012) and Gottardini et al. (2010) is used.

To develop a methodology which is able to predict AOT40 in inhomogeneous terrains from cumulated ozone data provided by passive sampling, Piikki et al. (2009) suggested combined hourly temperature monitoring, because diurnal O_3 concentration range and diurnal temperature range were strongly correlated, both spatially and temporally, in southwest Sweden. The approach performed well in 24-h AOT40 estimations, while the 12-h estimations were more dependent on site-specific parameterization. However, concurrent monitoring of climatic parameters such as temperature may be expensive and challenging at remote locations. This is why we applied a multi-variate, non-linear statistical approach (GRM) to geographical attributes that can be easily derived from GIS application. The results provided a better estimation of the AOT40 values than that obtained by the Loibl-based approach. A similar statistical approach was successfully applied

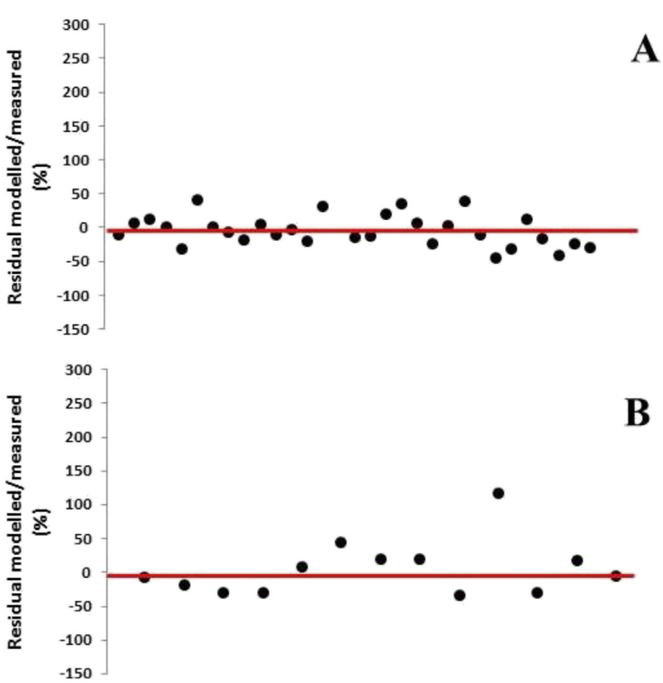


Fig. 4. Residuals (%) between AOT40 values modelled by GRM and AOT40 values calculated from hourly measurements ($AOT40_{meas}$) at suburban (A) and rural (B) stations for the 30% of data not used to build the GRM models. The *x*-axis represents the monitoring stations. A red line shows null percentage variation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to mimic the hourly frequency distributions of continuous measurements from passive O_3 sampling at two forest sites in Pennsylvania, USA (Krupa et al., 2003). In such an approach, however, only climatic variables were used, i.e. air temperature, relative humidity, precipitation, solar radiation, and wind speed. A high predictive relevance of a GRM approach was also reported for the estimation of Net Primary Productivity in Mediterranean forests (De Marco et al., 2013).

The three new functions obtained by the GRM analysis showed an excellent prediction capacity, as suggested by the high slope values in the cross-validation (Fig. 3). This improved estimation of AOT40 from biweekly values relative to the Loibl approach is due to the higher number of variables included in the GRM models, which took into account atmospheric O_3 concentration, as well as other geographical parameters (such as location, and distance from the sea and from the urban site), that are so critical in influencing AOT40. The AOT40 values were strongly dependent on physical predictors (latitude and longitude, alone or in combination with other predictors, like cumulated ozone and relative elevation). The GRM models suggest that cumulated ozone (O_3cum, i.e. the sum of the biweekly O_3 averages over the growing season) was the most important driver in determining AOT40 values, because it was the only parameter included in all the three equations. Elevation was important only when combined with other parameters, such as longitude or urban distance for the rural areas, whilst it was never an important predictor in the suburban areas. Although O_3 concentrations are known to increase with increasing elevation (Lovett and Kinsman, 1990) and therefore elevation was indicated as a major driver in AOT40 estimation (Loibl et al., 1994), our results suggest that other important geographical factors should be taken into account when AOT40 is estimated in terrains characterised by serious differences in climate and orography. These factors are distance from the cities and from the coastline. The importance of urban distance was likely due to the highly polluted urban environment, that is a main source of O_3 precursors. Sea distance resulted to be a proxy for the effects of elevation and large water bodies on O_3 chemistry.

In conclusion, multi-variate, non-linear regression models worked better than the Loibl-based approach in estimating AOT40. The new functions derived from GRM can easily be applied to estimate AOT40 when only cumulated and average ozone data are available, thus allowing reliable AOT40 predictions in inhomogeneous terrains. Further work is recommended for testing this approach outside the conditions the functions were developed for.

Author contribution

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Acknowledgements

KU acknowledges the COST Action STSM-FP0903-7635 grant. This work was also supported by the LIFE project FO3REST (LIFE10 ENV/FR/208) and the French Minister for Agriculture, Food, Fisheries, Rural Affairs and Town and Country Planning (MAAPRAT), and was made possible thanks to the good cooperation and harmony between the project partners: ACRI-ST, GIEFS (Groupement International d'Etudes des Forêts Sud-européennes), IPSP-CNR (Consiglio Nazionale delle Ricerche - Istituto per la Protezione Sostenibile delle Piante) and ENEA (Italian National Agency for New Technologies, Energy and Sustainable Economic Development).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2014.06.021.

References

BRACE, 2006. Dati e metadati di qualita' dell'aria. www.brace.sinanet.apat.it/web/struttura.html.

CMA, 2006. Unita' di ricerca per la climatologia e la meteorologia applicate all'agricoltura. Banca dati agrometeorologica nazionale. www.ucea.it.

Cox, R.M., 2003. The use of passive sampling to monitor forest exposure to O_3, NO_2 and SO_2: a review and some case studies. Environ. Pollut. 126, 301–311.

Cox, R.M., Malcolm, J.W., 1999. Passive ozone monitoring for forest health assessment. Water, Air Soil. Pollut. 116, 339–434.

De Marco, A., Screpanti, A., Paoletti, E., 2010. Geostatistics as a validation tool for setting ozone standards for durum wheat. Environ. Pollut. 30, 1–7.

De Marco, A., Screpanti, A., Attorre, F., Proietti, C., Vitale, M., 2013. Assessing ozone and nitrogen impact on net primary productivity with a generalised non-linear model. Environ. Pollut. 172, 250–263.

Di Baccio, D., Castagna, A., Paoletti, E., Sebastiani, L., Ranieri, A., 2008. Could the differences in O3 sensitivity between two poplar clones be related to a difference in antioxidant defense and secondary metabolic response to O_3 influx? Tree Physiol. 28, 1761–1772.

EUROAIRNET, 1999. Criteria for EUROAIRNET, the EEA Air Quality Monitoring and Information Network. Technical Report 12. European Environment Agency.

Fares, S., Vargas, R., Detto, M., Goldstein, A.H., Karlik, J., Paoletti, E., Vitale, M., 2013. Tropospheric ozone reduces carbon assimilation in trees: estimates from analysis of continuous flux measurements. Glob. Change Biol. 19, 2427–2443.

Gerosa, G., Ferretti, M., Buffoni, A., Spinazzi, F., 2003. Vegetation exposure to ozone at the permanent monitoring plots of the CONECOFOR programme in Italy: estimating AOT40 by means of passive samplers. In: Ferretti, M., Bussotti, F., Fabbio, G., Petriccione, B. (Eds.), Ozone and Forest Ecosystems in Italy. Second Report of the Task Force on Integrated and Combined (I&C) Evaluation of the CONECOFOR Programme, Annali Istituto Sperimentale per la Selvicoltura 1999, vol. 30 (Suppl. 1), pp. 53–62 (Special issue).

Gerosa, G., Ferretti, M., Bussotti, F., Rocchini, D., 2007. Estimates of ozone AOT40 from passive sampling in forest sites in south-western Europe. Environ. Pollut. 145, 629–635.

Gerosa, G., Finco, A., Marzuoli, R., Ferretti, M., Gottardini, E., 2012. Errors in ozone risk assessment using standard conditions for converting ozone concentrations obtained by passive samplers in mountain regions. J. Environ. Monit. 14, 1703–1709.

Gibson, M.D., Guernsey, J.R., Beauchamp, S., Waugh, D., Heal, M.R., Brook, J.R., Maher, R., Gagnon, G.A., McPherson, J.P., Bryden, B., Gould, R., Terashima, M., 2009. Quantifying the spatial and temporal variation of ground-level ozone in the rural Annapolis valley, Nova Scotia, Canada using Nitrite-impregnated passive samplers. J. Air Waste Manag. Assoc. 59, 310–320.

Gottardini, E., Cristofori, A., Cristofolini, F., Ferretti, M., 2010. Variability of ozone concentration in a montane environment, northern Italy. Atmos. Environ. 44, 147–152.

Hoshika, Y., Omasa, K., Paoletti, E., 2012. Whole-tree water use efficiency is decreased by ambient ozone and not affected by O_3-induced stomatal sluggishness. PLoS One 7 (6), e39270. http://dx.doi.org/10.1371/journal.pone.0039270.

Krupa, S.V., Legge, A., 2000. Passive sampling of ambient, gaseous air pollutant: an assessment from an ecological perspective. Environ. Pollut. 107, 31–45.

Krupa, S.V., Nosal, M., 9 April 2001. Relationships between passive sampler and continuous ozone (O_3) measurement data in ecological effects research. In: Bytnerowicz, A., Krupa, S., Cox, R. (Eds.), Proc. International Symposium on Passive Sampling of Gaseous Air Pollutants in Ecological Effects Research, Mission Inn, Riverside, CA, pp. 593–601. USDA Forest Service, Pacific Southwest Research Station, Air Pollution and Climate Impacts on Western Forest Ecosystems, Riverside, CA.

Krupa, S.V., Nosal, M., Peterson, D.L., 2001. Use of passive ozone (O_3) samplers in vegetation effects assessment. Environ. Pollut. 112, 303–309.

Krupa, S.V., Nosal, M., Ferdinand, J.A., Stevenson, R.E., Skelly, J.M., 2003. A multivariate statistical model integrating passive sampler and meteorology data to predict the frequency distributions of hourly ambient ozone (O_3) concentrations. Environ. Pollut. 124, 173–178.

Loibl, W., Winiwarter, W., Kopsca, A., Zueger, J., Baumann, R., 1994. Estimating the spatial distribution of ozone concentrations in complex terrain. Atmos. Environ. 28, 2557–2566.

Loibl, W., Bolhàr-Nordenkampf, H.R., Herman, F., Smidt, S., 2004. Modelling critical levels of ozone for the Forested area of Austria modifications of the AOT40 Concept. Sci. Pollut. Res., 1–10.

Lovett, G.M., Kinsman, J.D., 1990. Atmospheric pollutant deposition to high-elevation ecosystems. Atmos. Environ. Part A. General. Top. 24, 2767–2786.

Mazzali, C., Angiolino, E., Gerosa, G., Ballarin-Denti, A., 2002. Ozone risk assessment and mapping in the Alps based on data from passive samplers. Proceedings of the international symposium on passive sampling of gaseous air pollutants in ecological effects research. Sci. World J. 2, 1023–1035.

Matyssek, R., Bytnerowicz, A., Karlsson, P.-E., Paoletti, E., Sanz, M., Schaub, M., Wieser, G., 2007. Promoting the O_3 flux concept for European forest trees. Environ. Pollut. 146, 587–607.

Myers, R.H., Montgomery, D.C., 1995. Response Surface Methodology. John Wiley & Sons, Inc., NewYork.
Paoletti, E., Manning, W.J., 2007. Toward a biologically significant and usable standard for ozone that will also protect plants. Environ. Pollut. 150, 85–95.
Paoletti, E., de Marco, A., Beddows, D.C.S., Harrison, R.M., Manning, W.J., 2014. Ozone levels in European and USA cities are increasing more than at rural sites, while peak values are decreasing. Environ. Pollut. Available online 3 June 2014 (in press) http://dx.doi.org/10.1016/j.envpol.2014.04.040.
Papanastasiou, D.K., Melas, D., 2009. Climatology and impact on air quality of sea breeze in an urban coastal environment. Int. J. Climatol. 29, 305–315 http://dx.doi.org/10.1002/joc.1707.
Piikki, K., Klingberg, J., Pihl Karlsson, G., Karlsson, P.E., Pleijel, H., 2009. Estimates of AOT ozone indices from time-integrated ozone data and hourly air temperature measurements in southwest Sweden. Environ. Pollut. 157, 3051–3058.
Ribas, A., Peñuelas, J., 2006. Surface ozone mixing ratio increase with altitude in a transect in the Catalan Pyrenees. Atmos. Environ. 40, 7308–7315.
Sanz, M.J., Calatayud, V., Sánchez-Peña, G., 2007. Measures of ozone concentrations using passive sampling in forests of South Western Europe. Environ. Pollut. 145, 620–628.
Schaub, M., Emberson, L., Buker, P., Krauchi, N., 2007. Preliminary results of modeled ozone uptake for *Fagus sylvatica* L. trees at selected EU/UN-ECE intensive monitoring plots. Environ. Pollut. 145, 636–643.
Schaub, M., Calatayud, V., Ferretti, M., Brunialti, G., Lovblad, G., Krause, G., Sanz, M.J., 2010. Monitoring of air quality. 13 pp. Part XV. In: Manual on Methods and Criteria for Harmonized Sampling, Assessment, Monitoring and Analysis of the Effects of Air Pollution on Forests. UNECE, ICP Forests Programme Co-ordinating Centre, Hamburg, ISBN 978-3-926301-03-1.
Sicard, P., De Marco, A., Troussier, F., Renou, C., Vas, N., Paoletti, E., 2013. Decrease in surface ozone concentrations at Mediterranean remote sites and increase in the cities. Atmos. Environ. 79, 705–715.
Sundberg, J., Karlsson, P.E., Schenk, L., Pleijel, H., 2006. Variation in ozone concentration in relation to local climate in south-west Sweden. Water, Air Soil. Pollut. 173, 339–354.
Tuovinen, J.P., 2000. Assessing vegetation exposure to ozone: properties of the AOT40 index and modifications by deposition modelling. Environ. Pollut. 109, 361–372.
Tuovinen, J.P., 2002. Assessing vegetation exposure to ozone: is it possible to estimate AOT40 by passive sampling? Environ. Pollut. 119, 203–214.
UNECE, 2010. Mapping Manual: UNECE Convention on Long-range Transboundary Air Pollution. Chapter III Mapping Critical Levels for Vegetation, pp. 52.
Zhang, L., Jacob, D.J., Boersma, K.F., Jaffe, D.A., Olson, J.R., Bowman, K.W., Worden, J.R., Thompson, A.M., Avery, M.A., Cohen, R.C., Dibb, J.E., Flocke, F.M., Fuelberg, H.E., Huey, L.G., Mcmillan, W.W., Singh, H.B., Weinheimer, A.J., 2008. Transpacific transport of ozone pollution and the effect of recent Asian emission increases on air quality in North America: an integrated analysis using satellite, aircraft, ozonesonde, and surface observations. Atmos. Chem. and Phys. Discuss. 8, 8143–8191.