environmental sciences
proceedings

Proceeding Paper

Evaluation of the Simulated Atmospheric Particulate Matter Chemical Composition in Athens: Organic Aerosols Formation Sensitivity Tests †

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† Presented at the 16th International Conference on Meteorology, Climatology and Atmospheric Physics—COMECAP 2023, Athens, Greece, 25–29 September 2023.

Abstract: Air quality simulations were performed for the Greater Athens Area in very high spatial resolution using the modeling system WRF-CAMx. Sensitivity runs were performed using the SOAP and VBS schemes for organic gas–aerosol partitioning and oxidation. In January 2019, OA-VBS decreased compared to OA-SOAP because of POA reduction. In July 2019, the OA-VBS increased with respect to OA-SOAP as a result of the increase in SOA levels exceeding the decrease in POA ones. The comparison of the WRF-CAMx results against PM_{10}, $PM_{2.5,}$ and OC surface measurements provides the first indications for improved CAMx performance with the VBS scheme.

Keywords: PM atmospheric modeling; organic aerosols; CAMx; SOAP; VBS

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Citation: Poupkou, A.; Kontos, S.; Liora, N.; Tsiaousidis, D.; Kapsomenakis, I.; Solomos, S.; Liakakou, E.; Athanasopoulou, E.; Grivas, G.; Diapouli, E.; et al. Evaluation of the Simulated Atmospheric Particulate Matter Chemical Composition in Athens: Organic Aerosols Formation Sensitivity Tests. *Environ. Sci. Proc.* **2023**, *26*, 32. https://doi.org/10.3390/environsciproc2023026032

Academic Editors: Konstantinos Moustris and Panagiotis Nastos

Published: 24 August 2023

1. Introduction

Organic aerosols (OA) represent an important share of particulate matter (PM) concentrations ranging from 20 to 90% [1]. Chemical transport models (CTM) tend to underestimate mostly the secondary organic aerosols (SOA) [2]. Originally OA schemes in CTM assumed that the primary organic aerosols (POA) are non-volatile and chemically inert. This is the case for the secondary organic aerosol processor (SOAP) scheme [3], which accounts for the formation of the secondary organic aerosols (SOA) species that exist in equilibrium with condensable gasses produced by volatile organic compounds (VOC) oxidation. Photolytic loss of SOA is included in the SOAP scheme.

However, the POA was found to be mostly semi-volatile, and the vapor phase can undergo oxidation [4]. For this reason, the volatility basis set (VBS) approach was developed and implemented in CTM [5]. VBS provides a unified framework for gas–aerosol partitioning and chemical aging of both POA and SOA. It uses a set of semi-volatile OA species with volatility equally spaced in a logarithmic scale. The VBS species can react further in the atmosphere changing volatility.

The impact of using different organic aerosol schemes in the performance of CTM is still under investigation, depending on, among other things, the characteristics of the study area and the time period of the year simulated, in addition to the parameterizations applied in the schemes (mostly for VBS). According to a CTM evaluation study for Italy, the SOAP scheme shows a better performance than VBS, although VBS allows a better repartition of POA and SOA than the SOAP scheme [6]. A considerable improvement in the modeled OA mass, compared to previous model applications, has been found in Europe when implementing a modified VBS scheme [7]. The use of the VBS approach to simulate aerosols over Europe (May 2008) has led to improved OA predictions [8].

In this study, the model CAMx (v7.2) [9] was applied in very high spatial resolution for the largest urban center of Greece, Athens, and its performance on PM_{10}, $PM_{2.5}$, and OA simulation was compared when using two different OA gas–aerosol partitioning and oxidation schemes.

2. Materials and Methods

The modeling system comprised of the meteorological model WRF [10] and the photochemical model CAMx was applied over three nested domains covering Europe and North Africa (in 18 km), the Eastern Mediterranean (in 6 km), and the Greater Athens Area (GAA) (in 1.2 km). The simulations referred to cold and warm periods of the year 2019, i.e., January and July, respectively.

Anthropogenic gaseous and particulate matter emissions were obtained from the most recent CAMS-REGv5 emissions database [11]. A detailed emission inventory for the GAA was prepared, including bottom-up emissions for the heating and road transportation (exhaust and non-exhaust) sectors calculated on the basis of activity data and WRF meteorology [12]. Natural emissions included in the simulations refer to sea salt, windblown dust, and biogenic NMVOC and were calculated using the natural emissions model NEMO [13,14]. The WRF and CAMx models were driven by boundary conditions from the ERA5 reanalysis data and the CAMS-IFS global model [15], respectively.

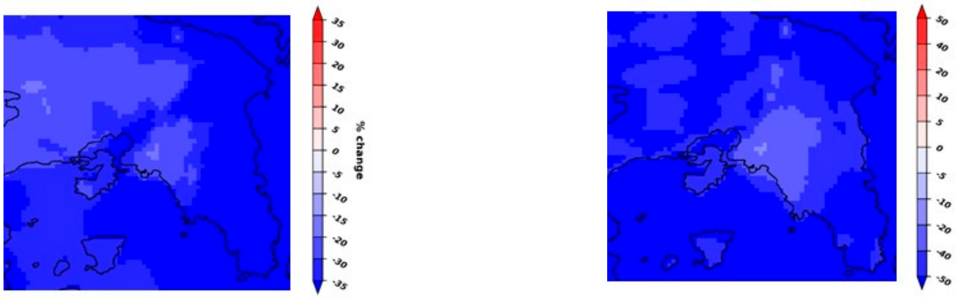
Sensitivity runs were performed and compared with CAMx using the SOAP2.2 and 1.5DVBS schemes for organic gas–aerosol partitioning and oxidation [9]. Intermediate-volatility organic compounds (IVOC) emissions need to be provided in CAMx simulations with the VBS scheme, in addition to the traditional anthropogenic and biogenic NMVOC used by SOAP. IVOC are important SOA precursors and were assumed as 1.5 times of POA [4].

The PM modeled results were evaluated against in situ surface measurements from (a) the monitoring network of the Ministry of Environment and Energy (MEEN) (https://ypen.gov.gr/, accessed on 24 February 2023) measuring PM_{10} and $PM_{2.5}$ concentrations, (b) the PANACEA research monitoring network (https://panacea-ri.gr/, accessed on 24 February 2023) including, in Athens, two urban background stations (i.e., Thissio and Demokritos), operated, respectively, by the National Observatory of Athens (NOA) [16] and by the N.C.S.R. "Demokritos" [17], which provide $PM_{2.5}$ chemical components concentrations, and (c) the PANACEA monitoring network of low-cost $PM_{2.5}$ sensors (https://air-quality.gr/, accessed on 24 February 2023), which in the GAA has been operated by NOA since July 2019 [18]. For validation purposes, the following evaluation metrics were estimated: normalized mean bias (NMB), normalized mean square error (NMSE), index of agreement (IOA), factor of 2 (Fac2), fractional bias (Fb), and fractional standard deviation (Fs). Desert dust transported over the study area may represent a high share of the PM atmospheric load [19], so these days were excluded from the analysis.

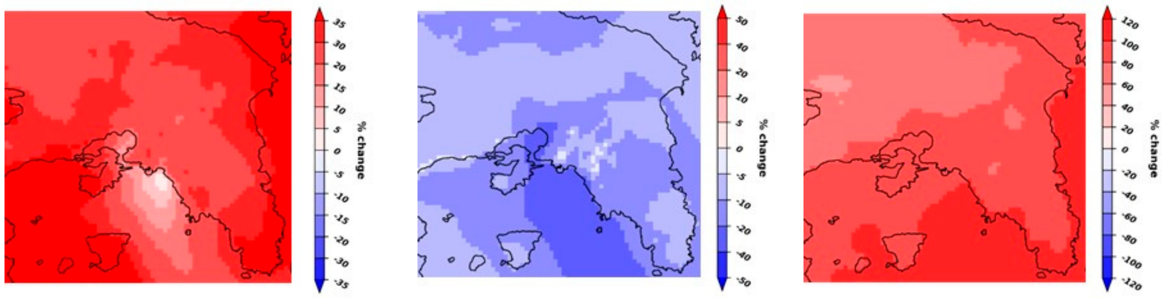
3. Results and Discussion

The different OA schemes introduce rather important differences in modeled POA and SOA values (Figure 1). In January 2019, the OA represented a high share of the total $PM_{2.5}$ mass in agreement with previous atmospheric composition studies for the urban background locations in the GAA [20], and the OA modeled with VBS decreased by 20–35%

than those with SOAP in the urban and suburban areas of the GAA (Figure 1a). The lower OA-VBS are related to POA reductions (Figure 1b), which can reach the order of 50% since POA are treated as volatile and undergoing aging processes in VBS. In July 2019, the contribution of OA to the total $PM_{2.5}$ mass was less pronounced than in January, and the OA-VBS increase, mainly between 20 and 30%, with respect to OA-SOAP in the urban and suburban areas of the GAA (Figure 1c). This increase is configured by the decrease of POA (Figure 1d) and the increase of SOA levels (Figure 1e).



(**a**) OA Jan 2019 (**b**) POA Jan 2019



(**c**) OA Jul 2019 (**d**) POA Jul 2019 (**e**) SOA Jul 2019

Figure 1. Percentage difference in simulated monthly concentration values between VBS and SOAP schemes for (**a**,**b**) OA, POA in January 2019 and (**c**–**e**) OA, POA, SOA in July 2019.

The evaluation metrics' average values for PM_{10} and $PM_{2.5}$ are presented in Table 1 by the different OA schemes used in CAMx runs. The overall performance of the modeling system can be considered quite satisfactory since most of the evaluation metrics take average values that fall within the acceptance criteria limit values [21–23]. The agreement between modeled and measured PM_{10} and $PM_{2.5}$ is better with the VBS scheme than with SOAP since the metrics values are improved. For example, mean reductions of NMB and NMSE are estimated to be 35% (41%) and 4% (7%), respectively, for PM_{10} ($PM_{2.5}$) in January 2019. NMB and NMSE decreased on average by 7% (12%) and 9% (12%), respectively, for PM_{10} ($PM_{2.5}$) in July 2019. These results are indicative of larger improvements with the use of the VBS OA scheme in wintertime than in summertime.

The comparison of simulated organic carbon (OC) concentrations (scaled from simulated OA using a factor equal to 1.6) with OC observations at the PANACEA stations also reveals that the VBS scheme outperforms the SOAP one since it reduces: (a) the model overestimation in the cold period studied (NMB is reduced by 38% in Thissio station) and (b) the model underestimation in the warm period studied (NMB is reduced by 11% in Thissio and by 18% in Demokritos stations) (Figure 2). Similarly, the warm period results for OA predictions in Finokalia (Greece) were improved when the original SORGAM (OA aging excluded) was replaced by the VBS scheme [8].

Table 1. Comparison between modeled and observed PM concentrations by different OA schemes.

	PM_{10} *				**$PM_{2.5}$ ***				**$PM_{2.5}$ ****	
	Jan 2019		**Jul 2019**		**Jan 2019**		**Jul 2019**		**Jul 2019**	
Evaluation Metrics * (Uniteless)**	**SOAP**	**VBS**	**SOAP**	**VBS**	**SOAP**	**VBS**	**SOAP**	**VBS**	**SOAP**	**VBS**
NMB	**+0.39**	**+0.25**	**−0.35**	**−0.33**	**+0.41**	**+0.21**	**−0.41**	**−0.38**	**−0.19**	**−0.14**
NMSE	1.42	1.31	0.57	**0.50**	1.71	1.50	0.71	0.62	**0.35**	**0.30**
IOA	**0.58**	**0.58**	0.48	**0.50**	**0.56**	**0.59**	0.43	0.44	0.44	0.46
Fac2	**0.59**	**0.62**	**0.65**	**0.69**	**0.58**	**0.61**	**0.60**	**0.65**	**0.78**	**0.81**
Fb	**+0.25**	**+0.15**	**−0.44**	**−0.41**	**+0.26**	**+0.13**	−0.54	**−0.48**	**−0.22**	**−0.16**
Fs	**+0.20**	**+0.07**	**−0.20**	**−0.21**	**+0.33**	**+0.17**	**−0.47**	**−0.46**	**−0.05**	**−0.03**

* Hourly measurements from the MEEN monitoring network (10 PM_{10} and 6 $PM_{2.5}$ stations). ** Hourly measurements from the low-cost $PM_{2.5}$ sensors of the PANACEA network in the GAA (seven locations). *** The values in bold are within the limit values indicating satisfactory model performance [21–23].

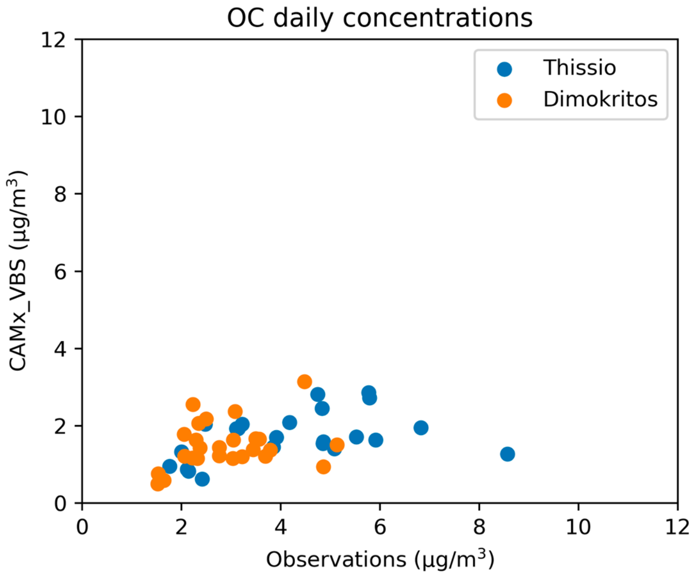


Figure 2. Comparison of observed and simulated with VBS scheme OC daily concentrations in July 2019.

4. Conclusions

The first results from the application of the high-resolution modeling system WRF-CAMx in the GAA have revealed its overall satisfactory performance being improved with the use of the VBS OA scheme with respect to the SOAP one. PM overestimation by CAMx during the cold period of the year is related mostly to OA values and provides an indication for adjustments in the estimated bottom-up biomass burning emissions. Future work will involve the validation of the modeling system on a winter/summer seasonal basis.

Author Contributions: Conceptualization, A.P. (Anastasia Poupkou); methodology, A.P. (Anastasia Poupkou), S.K. and N.L.; software, S.K., N.L. and D.T.; validation, A.P. (Anastasia Poupkou), S.K., N.L., D.T., I.K. and S.S.; data curation, E.L., E.A., G.G., E.D., V.V., S.P. and A.P. (Athena Progiou); writing, A.P. (Anastasia Poupkou).; review, C.Z., D.M., P.K., E.G., K.E. and A.P. (Athena Progiou). All authors have read and agreed to the published version of the manuscript.

Funding: The authors would like to acknowledge the support of the EU project, titled “Copernicus Atmosphere Monitoring Service CAMS2_82: Evaluation and quality control (EQA) of Global products”.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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