H14-144

BIOGENIC EMISSIONS IMPACT ON THE ATMOSPHERIC COMPOSITION IN BULGARIA

Georgi Gadzhev[1], Kostadin Ganev[1], Maria Prodanova[2], Dimiter Syrakov[2], Nikolay Miloshev[1]

[1] National Institute of Geophysics, Geodesy and Geography, Bulgarian Academy of Sciences, Bulgaria
[2] National Institute of Meteorology and Hydrology, Bulgarian Academy of Sciences, Bulgaria

Abstract: The present work aims at studying the role of biogenic emissions in local to regional atmospheric pollution transport and transformation processes over Bulgaria and at tracking and characterizing their impact on the main pathways that lead to atmospheric composition formation in the region.

The study is based on a large number of numerical simulations carried out for the summer period for two emission scenarios – with all the emissions and with biogenic emissions excluded. The US EPA Model-3 system is chosen as a modelling tool. The system consists of three components: MM5 - the 5th generation PSU/NCAR Meso-meteorological Model used as meteorological pre-processor; CMAQ - the Community Multiscale Air Quality System CMAQ; SMOKE - the Sparse Matrix Operator Kernel Emissions Modelling System – the emission model. As the NCEP Global Analysis Data with 1 degree resolution is used as meteorological background, the MM5 and CMAQ nesting capabilities are applied for downscaling the simulations to a 3 km resolution over Bulgaria. The TNO emission inventory is used as emission input. Special pre-processing procedures are created for introducing temporal profiles and speciation of the emissions. The biogenic emissions of VOC are estimated by the model SMOKE.

Some results from both emission scenarios which make it possible to evaluate the contribution of biogenic emissions in many different terms – spatial pattern, averaged over Bulgaria, seasonal behaviour, etc. are demonstrated in the paper.

Key words: *air pollution modelling, US EPA models-3 system, multi-scale modelling, biogenic emissions, emission scenarios*

INTRODUCTION

Regional studies of the air pollution over the Balkans, including country-to-country pollution exchange, had been carried out for quite a long time - see for example Syrakov et al. (2002), Ganev et al. (2003, 2008), Zerefos et al. (2000), Chervenkov (2006), Poupkou et al. (2008), Symeonidis et al. (2008), Zanis et al. (2007). These studies were focused on both studying some specific air pollution episodes and long-term simulations and produced valuable knowledge and experience about the regional to local processes that form the air pollution pattern over Southeast Europe. It seems, however, that the impact of the biogenic emissions on the air pollution of the Balkan Peninsula as a whole had never been comprehensively studied. Carrying out such a comprehensive study with up-to-date modelling tools detailed and reliable input data for long enough simulation periods and good resolution is the aim of the present work.

It should be noted that the Balkan Peninsula is a region with complex topography, which causes significant disturbances of the air flows. These mesoscale disturbances may have a great influence not only on the local pollution transport and hence on the detailed pollution pattern, but also on the trans-boundary transport of substances (see for example Rappenglück, B. et al., 2003, Melas, D. et al., 2000, Ganev et al., 2008). That is why the multi-scale modeling is an important issue in the numerical experiments strategy.

APPROACHES, TOOLS, DATA, DOMAINS AND NESTING

All the simulations are based on the US EPA Model-3 system. The system consists of three components: MM5 (Dudhia, 1993, Grell et al., 1994), used as meteorological pre-processor, **CMAQ** (Byun et al., 1998, Byun and Ching, 1999), the Chemical Transport Model of the system and **SMOKE** (CEP, 2003) – the emission pre-processor of Models-3 system.

The large scale (background) meteorological data used by the study is the NCEP Global Analysis Data with 1º×1º resolution. At the moment the created database contains all the necessary information since year 2000.

The TNO high resolution emission inventory (A. Visschedijk et all., 2007) is exploited. The TNO inventory resolution is 0.25°×0.125° longitude-latitude. The inventory contains 8 pollutants: CH_4, CO, NH_3, NMVOC (VOC), NO_x, SO_x, PM10 and PM2.5, distributed over 10 SNAP categories. The biogenic emissions, which depend on the vegetation type and the meteorological conditions, are calculated by the SMOKE model.

The emission inventory is made on annual basis and many pollutants are estimated as groups like VOC and PM2.5. In preparing CMAQ emission file, a number of specific estimates must be done. First, all this information must be gridded. Secondly, time variation profiles must be over-posed on these annual values to account for seasonal, weekly and daily variations. Finally, VOC and PM2.5 emission estimates must be split into more defined compounds in order to be properly modeled for chemical transformations and deposition ("speciation").

The temporal allocation is made on the base of daily, weekly and monthly profiles, provided by (Builtjes et al., 2003). A specific approach for obtaining speciation profiles is used here. The USA EPA data base is intensively exploited. A Bulgarian emission expert has found coincidence between main Bulgarian sources for every SNAP with similar source types from US EPA nomenclature. The weighted averages of the respective speciation profiles are accepted as SNAP-specific splitting factors, weights being the percentage of contribution of every source type in total Bulgarian emission in particular SNAP. In such a way VOC and PM2.5 speciation profiles are derived.

As far as the background meteorological data is the NCEP Global Analysis Data with 1º×1º resolution, it is necessary to use MM5 and CMAQ nesting capabilities as to downscale to 3 km step for the innermost domain. The MM5 pre-processing program TERRAIN was used to define four domains with 81 (D1), 27 (D2), 9 (D3) and 3 (D4) km horizontal resolution. These four nested domains were chosen in such a way that the finest resolution domain contains the whole territory of Bulgaria and the domain with a horizontal resolution of 9 km contains the whole Balkan Peninsula.

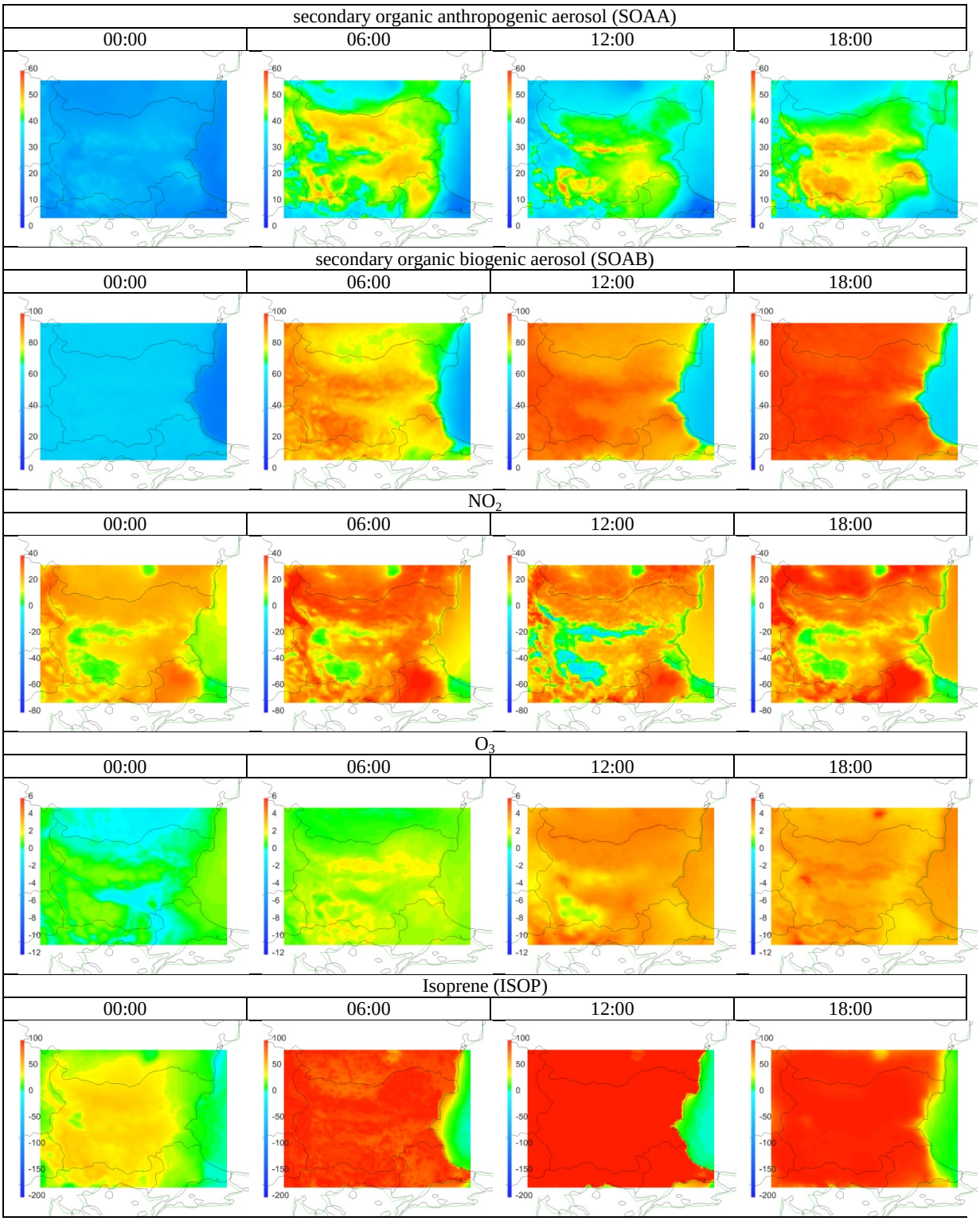

Figure 10. Plots of the biogenic emissions relative contribution [%] to SOAA, SOAB, NO_2, O_3 and ISOP summer surface concentrations in D4 in 00:00, 06:00, 12:00 and 18:00 GMT.

Performing extensive simulations with up to date highly sophisticated numerical models obviously requires computer resources of the order of magnitude of those provided by the so-called supercomputers. Using supercomputers, however, is

rather expensive and far beyond what most of the research groups can afford. Luckily an alternative technology – the grid computing (Atanassov et all., 2006, Foster and Kesselmann, 1998, Ganev et all., 2009), is recently very intensively developing, which makes formulating and solving problems absolutely unthinkable several years ago already quite relevant.

SOME EXAMPLES FROM THE NUMERICAL EXPERIMENTS

Brief Description of the Numerical Experiment

The meteorological pre-processor MM5 was forced by the NCEP global scale data. In the D1 domain the model was set to relax toward observed temperature, wind and humidity through four dimensional data assimilation (FDDA) (Stauffer and Seaman, 1990). FDDA amounts to adding an additional term to the prognostic equations that serves to "nudge" the model solution toward the individual observations. This significantly reduces the drift in the solution for simulations of several days or more. The NCEP data set does not include observations, but analyzed data every 6 hours in all its grid points. MM5 is configured with FDDA option on as to nudge the model toward analyzed data in D1 only. For all the domains (D1, D2, D3, D4) was run simultaneously with "two-way" nesting mode on. All simulations were made with 23 σ-levels going up to 100 hPa height. The MM5 simulations were made on portions of 3 days. Every portion has additional 12 hours that are an initial spin-up period that overlaps the last 12 hours of the preceding run.

CMAQ meteorological input was created from the MM5 output exploiting the CMAQ meteorology-chemistry interface - MCIP, v2.3. CMAQ simulations were performed in D2, D3 and D4 domains. The CMAQ pre-defined (default) concentration profiles were used as boundary conditions for D2. The boundary conditions for the inner domains were determined through the nesting capabilities of CMAQ. The CB-4 chemical mechanism with Aqueous-Phase Chemistry and MEBI solver has been exploited for all the domains. The CMAQ simulations were made with 15 σ-levels vertical resolution.

The MM5/CMAQ simulations were performed for 8 years - from 2000 to 2007, for 2 emission scenarios – with the biogenic emissions included and excluded respectively. The relative contributions of the biogenic emissions were calculated for each day of this 8 year period and then by averaging the typical fields of relative contribution of biogenic emissions to each of the compound surface (concentrations were calculated for the 4 seasons and annually.

Results, Comments and Discussion

The diurnal course of the biogenic emission contribution fields for secondary organic anthropogenic aerosol (SOAA), secondary organic biogenic aerosol (SOAB), NO_2 , O_3 and isoprene (ISOP) for the summer period is demonstrated in Figure 1. The following most general features of the biogenic emission contribution fields can be seen from the figures: very complex spatial distribution and well manifested diurnal course. It should be especially mentioned that the comparison of the pollution field patterns in D3 (which due to the limited paper volume will not be demonstrated here) and D4 shows that there is no significant qualitative differences due to the improved spatial resolution in D4.

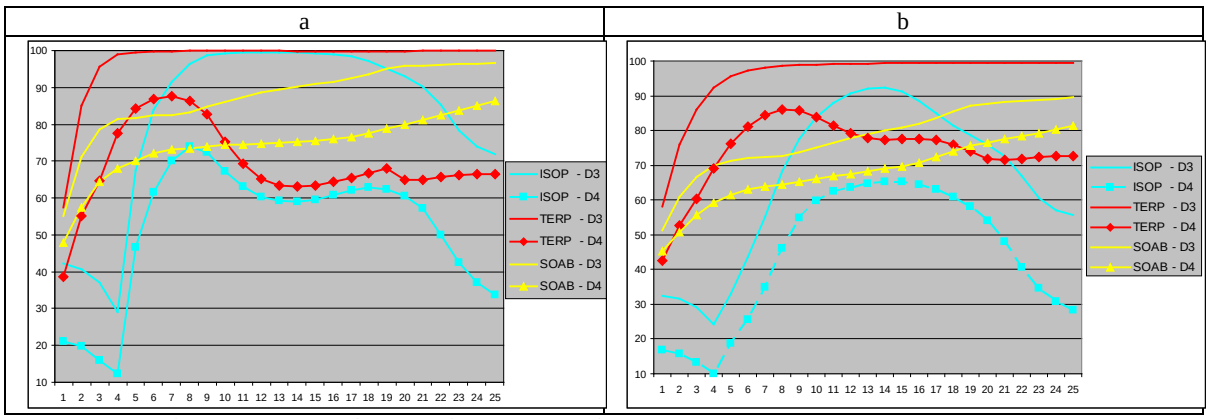

Figure 2. Plots of the diurnal course of averaged for the territory of Bulgaria biogenic emissions relative contributions [%] to Isoprene, Terpene and SOAB surface concentrations for the summer period (a) and annually (b).

Plots of this kind are rather spectacular and can give a good qualitative impression of the spatial complexity of the biogenic emission contribution. In order to demonstrate the biogenic emission contribution behavior in a more simple and easy to comprehend way, the respective fields can be averaged over some domain (in this case the territory of Bulgaria), which makes it possible to jointly follow and compare the diurnal behavior of the respective contributions for different species. Such plots for some of the compounds are given in Figures 2 – 5.

First of all it could be seen that the biogenic emissions relative contribution to the concentration of different species could be rather different, varying from almost 100 to several %. It can be also seen that the role of the spatial resolution is not negligible – there could be significant quantitative differences between the contributions, calculated in D3 (black lines) and D4 (white lines). Some quite obvious qualitative differences in particular in contribution diurnal course for Isoprene, Terpene and SOAB can also be seen. For example the contribution to Terpene concentrations, calculated in D3 reaches a 100% plateau early in the morning, while the behaviour in D4 is different – it reaches a maximum in 6-7 o'clock in the morning and then decreases.

Another general comment, which can be made, is that the annual contributions of biogenic emissions are, for almost all the species, much smaller than the one for summer. This is quite natural, of course, having in mind that in the warm period of the year the biogenic emissions are higher.

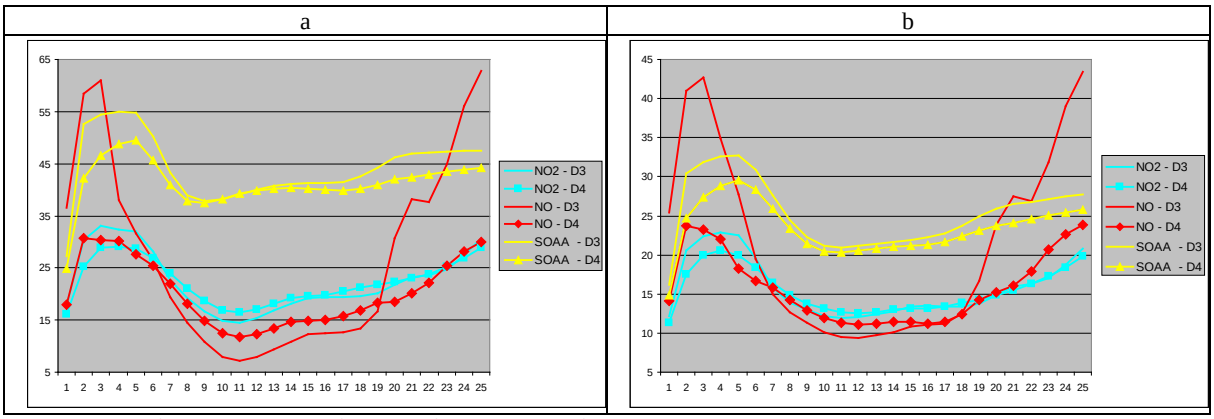

Figure 3. Plots of the diurnal course of averaged for the territory of Bulgaria biogenic emissions relative contributions [%] to NO_2, NO and SOAA surface concentrations for the summer period (a) and annually (b).

Some important qualitative differences in the contribution diurnal course for different species should also be mentioned: for Isoprene, Terpene, SOAB, O_3, and NH_3 they reach there maximal values in the morning or during the day, while for NO_2, NO, SOAA and PNH4 the biogenic emissions relative contributions have sinks at daytime. A very well displayed anti-correlation between contributions for NH_3 and PNH_4 can be observed.

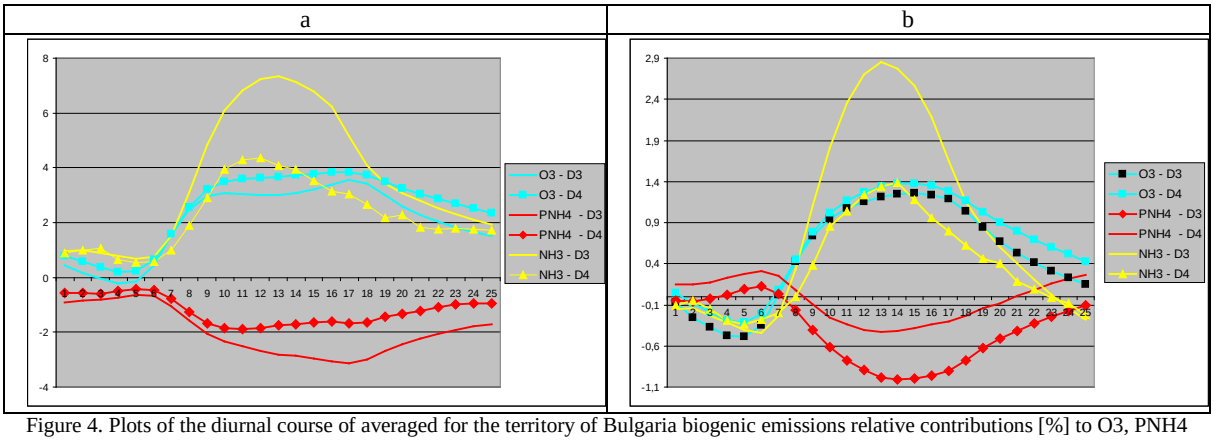

Figure 4. Plots of the diurnal course of averaged for the territory of Bulgaria biogenic emissions relative contributions [%] to O3, PNH4 (ammonium) and NH3 (ammonia) surface concentrations for the summer period (a) and annually (b).

One can not help but notice the small contribution of biogenic emissions to surface ozone. At first glance this may occur strange, moreover that the biogenic emissions contribution to major Volatile Organic Compounds (VOC) like Isoprene, Terpene is large and the VOCs are one of the major ozone precursors. This can be explained, however, by the ozone photochemistry (Finlayson-Pitts and Pitts Jr., 1986, Seinfeld and Pandis, 1998, Staehelin, Prévôt and Barnes, 2000), more precisely by the ROx/HOx radical chain reaction system: OH radicals can react (i) with organic compounds leading to peroxyradical formation which produces O_3 by oxidizing NO to NO_2 or (ii) OH can react with NO_2 forming HNO_3 which is a termination reaction suppressing O_3 formation. The dominance of pathway (i) over (ii) depends on the NO_2 concentration versus the sum of NM-VOCs concentrations in the air parcel (weighted over the reaction rates of the individual species). In urban environments NO_2 concentration are usually that large that HNO_3 formation dominates the reactions of OH radicals (pathway (ii)), which implies that local O_3 production is small. These conditions are also called ***VOC-limitation*** because O_3 production increases with increasing VOC concentration. When the air parcel moves along the trajectory from an urban to a suburban environment, NO_2 concentration in the air parcel steadily decreases because NO_2 reacts with the available OH radicals. The decrease in NO_2 changes the dominance of pathways (ii) over (i) favouring more pathway (i) and therefore local O3 production increases. When NO_x concentration is decreasing steadily the mixture of organic vs. NO_x concentration passes through a state in which the ratio of ozone precursor concentration is such that local O_3 production maximizes, which is called the ***transition regime***. When NO_x concentration is decreasing further (by pathway (ii)) local O_3 production rate becomes limited by the availability of NO_x concentration, a regime which is called ***NO_x-limitiation***. Such conditions usually occur in rural environments. Obviously from a point of view of atmospheric composition climate the Balkan Peninsula and Bulgaria are predominantly "rural" environment which explains the ozone photochemistry specifics in the region.

CONCLUSIONS

The biogenic emissions impact on atmospheric composition is far from comprehensively studied. The numerical experiments performed produced a huge volume of information, which have to be carefully analyzed and generalized so that some final

conclusions could be made. The obtained ensemble of numerical simulation results is extensive enough to allow statistical treatment – calculating not only the mean concentrations and biogenic emission contribution mean fields, but also standard deviations, skewness, etc. with their dominant temporal modes (seasonal and/or diurnal variations). Extreme situations and their relation with specific meteorological conditions could also be outlined. The CMAQ "Integrated Process Rate Analysis" could also be applied to reveal the role of different transport and transformation processes through which the biogenically generated species influent atmospheric composition.

ACKNOWLEDGMENTS

The present work is supported by the Bulgarian National Science Fund (grants № Д002-161/16.12.2008 and ДЦВП-02/1/29.12.2009). The work of the young scientist G. Gadzhev is also supported by the ESF project № BG51PO001-3.3.04-33/28.08.2009.

Deep gratitude is due to US EPA, US NCEP and EMEP for providing free-of-charge data and software. Special thanks to the Netherlands Organization for Applied Scientific research (TNO) for providing us with the high-resolution European anthropogenic emission inventory.

REFERENCES

Atanassov E., T. Gurov and A. Karaivanova, 2006: Computational Grid: structure and Applications, *Journal Avtomatica i Informatica* (in Bulgarian), year XL, September 2006, 40-43.

Builtjes P., M. van Loon, M. Schaap, S. Teeuwisse, A.J.H. Visschedijk and J.P. Bloos, 2003: Project on the modelling and verification of ozone reduction strategies: contribution of TNO-MEP, TNO-report, MEP-R2003/166, Apeldoorn, The Netherlands.

Byun, D., Ching, J., 1999: Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. *EPA Report 600/R-99/030*, Washington DC.

Byun, D., J. Young, G. Gipson, J. Godowitch, F.S. Binkowski, S. Roselle, B. Benjey, J. Pleim, J. Ching, J. Novak, C. Coats, T. Odman, A. Hanna, K. Alapaty, R. Mathur, J. McHenry, U. Shankar, S. Fine, A. Xiu, and C. Jang, 1998: Description of the Models-3 Community Multiscale Air Quality (CMAQ) Modeling System, *10th Joint Conference on the Applications of Air Pollution Meteorology with the A&WMA, 11-16 January 1998, Phoenix, Arizona*, 264-268.

Chervenkov Hr., 2006: Estimation of the Exchange of Sulphur Pollution in the Southeast Europe, *Journal of Environmental Protection and Ecology* vol.**7**, № 1, 10 – 18.

Dudhia, J. 1993: A non-hydrostatic version of the Penn State/NCAR Mesoscale Model: validation tests and simulation of an Atlantic cyclone and cold front. *Mon. Wea. Rev.* **121**, 1493-1513.

Finlayson-Pitts B. and J.N. Pitts Jr., 1986: Atmospheric Chemistry, John Wiley and Sons, New York.

Foster J., C. Kesselmann, 1998: The Grid: Blueprint for a New Computing Infrastructure, Morgan Kaufmann.

Ganev K., R. Dimitrova, D. Syrakov, Ch. Zerefos, 2003: Accounting for the mesoscale effects on the air pollution in some cases of large sulfur pollution in Bulgaria or Northern Greece, *Environmental Fluid Mechanics*, **3**, 41-53.

K. Ganev, M. Prodanova, D. Syrakov and N. Miloshev, 2008: Air pollution transport in the Balkan region and country-to-country pollution exchange between Romania, Bulgaria and Greece, *Ecological Modelling*, **217**, 255–269.

Ganev K., D. Syrakov, M. Prodanova, N. Miloshev, G. Jordanov, G. Gadzhev, and A. Todorova, 2009: Atmospheric composition modeling for the Balkan region, *SEE-GRID-SCI USER FORUM 2009, Istanbul, 9-10 December 2009*, ISBN:978-975-403-510-0, 77-87

Grell, G.A., Dudhia J., and Stauffer D.R., 1994: A description of the Fifth Generation Penn State/NCAR Mesoscale Model (MM5). NCAR Technical Note, NCAR TN-398-STR, 138 pp.

Poupkou, A., Symeonidis, P., Lisaridis, I., Melas, D., Ziomas, I., Yay, O.D., Balis, D. 2008: Effects of anthropogenic emission sources on maximum ozone concentrations over Greece, *Atmospheric Research*, **89** (4), 374-381.

Seinfeld J.H. and S. N. Pandis, 1998: Atmospheric Chemistry and Physics, John Wiley and Sons, New York.

Staehelin J., A.S.H. Prévôt and J. Barnes, 2000: Photochemie der Troposphäre, Handbuch der Umweltveränderungen und Ökotoxikologie, Band IA: Atmosphäre, R. Guderian, Ed., Springer Verlag, 207-341.

Symeonidis, P., Poupkou, A., Gkantou, A., Melas, D., Devrim Yay, O., Pouspourika, E., Balis, D., 2008: Development of a computational system for estimating biogenic NMVOCs emissions based on GIS technology *Atmospheric Environment*, **42** (8), 1777-1789.

Syrakov D., M. Prodanova, K. Ganev, Ch. Zerefos, A. Vasaras, 2002: Exchange of sulfur pollution between Bulgaria and Greece, *Environmental Science and Pollution Research*, v.9, No5, 321-326.

Visschedijk, A., Zandveld P., van der Gon, H., 2007: A high resolution gridded European emission database for the EU integrated project GEMS, TNO report 2007-A-R0233/B, The Netherlands

Zanis, P., Poupkou, A., Amiridis, V., Melas, D., Mihalopoulos, N., Zerefos, C., Katragkou, E., Markakis, K., 2007: Effects on surface atmospheric photo-oxidants over Greece during the total solar eclipse event of 29 March 2006, *Atmospheric Chemistry and Physics Discussions*, **7** (4), 11399-11428.

Zerefos C., K.Ganev, K.Kourtidis, M.Tzortziou, A.Vasaras, E.Syrakov, 2000: On the origin of SO2 above Northern Greece. *Geophysical Research Letters*, **27**, No.3, 365-368.