



www.atmospolres.com

# Air quality over Portugal in 2020

## Alexandra Monteiro, Joana Ferreira, Isabel Ribeiro, Ana Patricia Fernandes, Helena Martins, Carla Gama, Ana Isabel Miranda

CESAM & Department of Environment and Planning, University of Aveiro, 3810–193 Aveiro, Portugal

## ABSTRACT

This works intends to evaluate the impacts of the national emission ceilings (NEC) reduction scenarios on the air quality in Portugal, verifying the fulfillment of the air quality thresholds for 2020. The air quality numerical modeling system WRF–EURAD was applied to this 2020 future scenario and results were compared to the present situation – year 2012. This modeling system was already evaluated for Portugal domain in previous studies, by comparison with measured air quality data, and showed reasonable skills for all the pollutants. This system was applied over the Continental domain of Portugal, using nesting approach, with a horizontal resolution of 5x5 km<sup>2</sup>, for both scenarios conditions (2012 and 2020) considering the respective emissions data and assuming the 2012 meteorological conditions. The results point towards an improvement of the air quality over Continental Portugal, in particular for particulate matter (in the urban areas of Lisbon and Porto) and SO<sub>2</sub> (near specific industrial sources) but do not solve the mon–compliance status regarding the O<sub>3</sub> threshold value for protection of human health. These results strengthen the importance of including the NEC emission scenarios in the air quality national strategy, but additional mitigation actions need to be designed, with focus on ozone and its precursors, at local and regional scale.

Keywords: Air pollutants, national emission ceilings, 2020 scenario, air quality modeling



Corresponding Author: *Corresponding Manteira* 2 : +351-234-370-220 3 : +351-234-370-309 ⊠ : alexandra.monteiro@ua.pt

#### Article History:

Received: 04 November 2014 Revised: 25 February 2015 Accepted: 25 February 2015

doi: 10.5094/APR.2015.087

## 1. Introduction

Poor air quality is a major issue in Europe, both for public health, the economy and the environment. Significant progress has been achieved in the past 20 years in the European Union (EU) by a dedicated and common policy in the field of anthropogenic atmospheric emissions and air quality, including the "Thematic Strategy on Air Pollution" (COM(2005)446 final), the National Emission Ceilings (NEC) Directive (2001/81/EC), and the Directive 2008/50/EC on ambient air quality and cleaner air for Europe, among others.

The NEC Directive was adopted in 2001 in order to limit the negative environmental impacts of acidification, eutrophication and ground–level ozone, by establishing for each Member State for 2010 a cap on emissions of sulfur dioxide (SO<sub>2</sub>), nitrogen oxides (NO<sub>X</sub>), non–methane volatile organic compounds (NMVOC) and ammonia (NH<sub>3</sub>). Parallel to the development of the EU NEC Directive, the EU Member States together with Central and Eastern European countries, the United States and Canada have negotiated the "multi–pollutant" protocol under the Convention on Long–Range Transboundary Air Pollution (the so–called Gothenburg protocol, agreed in November 1999). Between 1990 and 2010, significant cuts on emissions of several air pollutants were achieved in the EU: SO<sub>2</sub> emissions by 56% and NH<sub>3</sub> emissions by 28% between 1990 and 2010 (EEA, 2014).

Despite improvements over several decades, air pollution continues to cause substantial human health impacts as a significant proportion of Europe's population live in cities, where exceedances of air quality standards regularly occur: 33% of the EU urban population lives in areas where the EU air quality 24–hour limit value for particulate matter ( $PM_{10}$ ) was exceeded in 2011, also between 14% and 65% of the EU urban population was exposed to ozone (O<sub>3</sub>) concentrations above the EU target value for protecting human health in the period 2002–2011 (EEA, 2013a). On the other hand, Europe's sustained ambient O<sub>3</sub> concentrations continue to cause considerable damage to vegetation growth and crop yields, with between 21% and 69% of European agricultural crops exposed to levels above the EU target value for protecting in growth and crop yields with between 21% and 69% of European agricultural crops exposed to levels above the EU target value for protecting vegetation from 2002 to 2010, resulting in serious costs to the Europe's economy and reducing plant uptake of carbon dioxide (EEA, 2013b).

The long-term strategic objective of the new European Clean Air Program, proposed by the European Commission in 2013, is to attain air quality levels that do not give rise to significant negative impacts on, or risks for, human health and the environment. In face of the challenges that have been found in complying with air quality standards, the first objective of the proposed Air Policy Package is to achieve full compliance with present air quality policies, and conform to international commitments by 2020. The second general objective of the European Clean Air Program is to reduce the impact of air pollution beyond 2020, with 2030 being the target year. For that a proposal for a revised National Emission Ceilings Directive has been prepared (COM(2013)920final), applicable from 2020 and 2030 for NO<sub>X</sub>, NMVOC, SO<sub>2</sub>, NH<sub>3</sub>, particulate matter (PM) and methane (CH<sub>4</sub>). To ensure timely compliance, interim targets applicable to the same pollutants will apply for 2025. The aim of the envisaged staggered tightening of commitments is to achieve compliance with the amended Gothenburg Protocol by 2020 (UNECE, 2012a; UNECE, 2012b). The revision builds upon the evaluation and review of the National Programs 2002 and 2006, the work performed under the Clean Air for Europe Program, the Thematic Strategy on Air Pollution, and the new scientific and technical work. The revision also takes into account (proposals for) the Community legislation for specific source categories, like Euro 5/6, EURO VI, the revision of the IPPC–directive and the decision of the European Council of March 2007 to reduce the greenhouse gas emissions by 20% and to have 20% renewables by 2020.

Although complying with the NEC Directive, with NO<sub>X</sub>, NMVOC, SO<sub>2</sub> and NH<sub>3</sub> emissions 32%, 6%, 65% and 47% respectively below the ceiling (EEA, 2014), Portugal is one of the European countries facing air quality problems with non-compliance of the legislation, exceeding in 2011 the annual limit value for PM<sub>10</sub> and NO<sub>2</sub>, as well as the target value threshold for O<sub>3</sub> (Monteiro et al., 2007; Monteiro et al., 2012; EEA, 2013c).

In order to analyze the efficiency of the national programs in complying with the present air quality policies and commitments by 2020, it is important to evaluate their effects on the air quality, taking into account the national reduction measures. In this sense, the main objective of this study was to verify the fulfillment of the air quality limit values for 2020 considering the National Emission Ceiling Scenarios, using the numerical air quality modeling system composed by the WRF meteorological model and the EURAD chemistry model, for both present 2012 and 2020 emission scenarios.

## 2. Air Quality Modeling

Numerical modeling has become a fundamental tool to support decision makers on air quality management due to its capacity to estimate atmospheric pollutants concentrations over the entire region of interest, taking into account complex and nonlinear physical and chemical mechanisms that characterize the atmosphere, as well as to evaluate the efficiency of emission scenarios (Ribeiro et al., 2014). A mesoscale numerical modeling system was selected and applied in the present study to

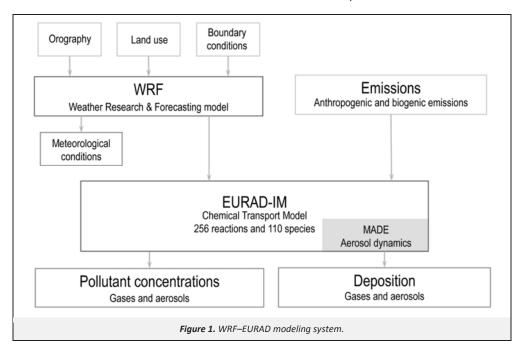
#### 2.1. The air quality modeling system

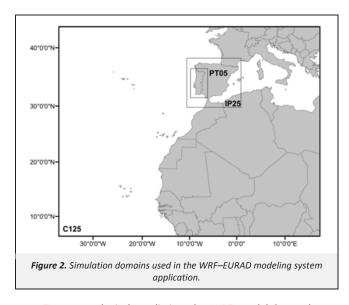
The air quality modeling system comprises the Weather Research & Forecasting (WRF, version 3.5.0) model (WRF, Skamarock et al., 2008) and the EURopean Air pollution Dispersion Chemistry Transport Model (EURAD–CTM), (Elbern et al., 2007). The WRF-EURAD is a comprehensive Eulerian air quality modeling system in a non-hydrostatic configuration. Its nesting facility enables to telescope from 1000 km to 1 km of horizontal resolution, allowing the combination of both high grid resolutions and the representation of large-scale transport processes. WRF and EURAD-CTM use a Lambert conformal conic projection grid with an equidistant rectangular horizontal spacing and the state variables are represented according to the Arakawa C-Grid staggering (Arakawa and Lamb, 1977). The EURAD-CTM, designed for simulations of oxidants and aerosol formation, needs emission input data and the WRF meteorological fields, according to the scheme of Figure 1.

#### 2.2. Air quality modeling setup and application

The WRF–EURAD simulations comprehend the application of three different spatial domains in order to reach a high–resolution scale over Portugal area, using nesting capabilities. At first, a grid with large extent, in a continental scale, covering Southern Europe with a low horizontal resolution of 125×125 km<sup>2</sup> (C125, the coarse domain); then a second domain covering Iberian Peninsula with 25×25 km<sup>2</sup> of horizontal resolution (IP25) and then the last high–resolution domain covers mainland Portugal, with 5×5 km<sup>2</sup> (PT05). The different simulation domains are geographically represented in Figure 2.

Regarding the vertical resolution, all the domains are divided into 23 terrain–following sigma coordinate layers. The top boundary of the WRF–EURAD is set at 100 hPa and the diffuse vertical fluxes at the top are set to zero. About 15 layers are defined above 2 km height and the Earth's surface defines the bottom boundary.





To meteorological prediction the WRF model has a large variety of physical parameterizations, which include microphysics, cumulus parameterization and radiation, land-surface and planetary boundary layer schemes. The parameterizations selection was based on recommendations included in Wang et al. (2014), as well as on validation and sensitivity studies previously performed over Portugal (Aquilina et al., 2005; Carvalho et al., 2006) and over the Iberian Peninsula (Fernandez et al., 2007). Table 1 compiles the parameterizations used in this work. The global meteorological fields from the National Center for Environmental Prediction (NCEP/NOAA, 2000), which provide final operational global data on 1° by 1° grids with a temporal resolution of six hours, were used to supply initial and boundary conditions for the coarse domain (C125), while for the other domains, the initial and boundary conditions come from the respective parent domain and from the previous simulated day. The land use data set from USGS24 was used within WRF simulations for C125 and IP25 domains, while for the PT05 simulation domain an upgrade based on the Corine Land Cover 2 000 for Portugal (Martins, 2012) was considered.

As a CTM, the EURAD simulates advection and diffusion, chemical conversion and deposition of trace gases and aerosols in the atmosphere thought solving mass conservation equation and

using the chemical and physical options compiled in Table 1. The set of the parameterizations used herein was recommended from the model developer (e.g., Nieradzik, 2011), as well as from previous studies performed over Portugal and the Iberian Peninsula (Borrego et al., 2011; Monteiro et al., 2013a).

This modeling system was applied for the 2012 and 2020 emission scenarios, considering for both cases the meteorological year of 2012 (same WRF model simulation). The use of present meteorology for 2020 simulations introduces additional uncertainties in the simulation results as it projected that surface temperature will rise over the 21st century under all assessed emission scenarios, being likely that heat waves will occur more often and last longer (IPCC, 2014). Simulations for 2020 climate are not readily available, as researchers focus their attention in medium and long-term simulations. A recent study produced a set of high resolution climate simulations for the Portuguese mainland, for three 20-year periods (historic (1986-2005), midterm (2046–2065), and long-term (2081–2100)) which indicated an increase in the P90 temperature between the mid-term and the historic simulation in the order of 3 to 4 °C over central and northern Portugal (Marta-Almeida et al., 2014). These results indicate that ozone concentrations may be exacerbated under future climate.

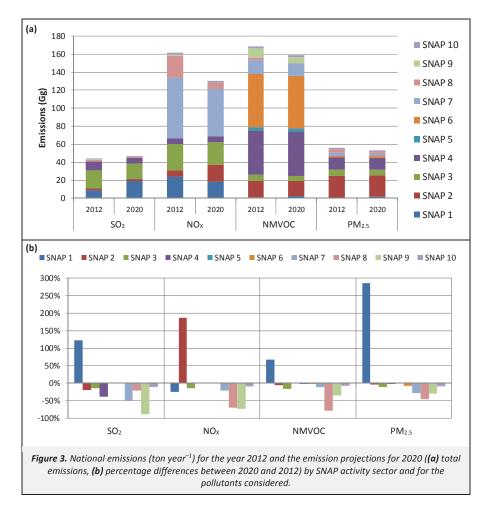
The emission data input is described in detail as follows.

## 3. Emission Data

In the scope of the national strategy for air quality for the period of 2014-2020, emission projections have been developed for 2020 based on a methodological approach consistent with the national submissions in the frame of the Portuguese Informative Inventory Report, on the Convention on Long-Range Transboundary Air Pollution, and on the Portuguese economic development scenarios till 2020 established in the scope of the National Plan for Climate Change (PNAC) (APA, 2014), including scenarios of demand for energy services, materials, and other activities and the policies and measures to be implemented till 2020. The emissions estimation addresses the pollutants nitrogen oxides (NO<sub>x</sub>), SO<sub>2</sub>, NMVOC and particulate matter (PM<sub>2.5</sub> and PM<sub>10</sub>). The emission totals by SNAP (Standardized Nomenclature for Air Pollutants; www.emep.int/) activity sector and by pollutant estimated for 2020 were compared to the national emission inventory for 2012, considered as the base year of this study. The results are presented in Figure 3.

Model	Physic and Chemical Parameters	Option
WRF	Microphysics	WSM 6-class Graupel scheme (Hong & Lim, 2006)
	Long- and shortwave radiation	Rapid Radiative Transfer Model scheme
	Land and surface schemes	Rapid Radiative Transfer Model scheme
	Land and surface schemes	Pleim–Xiu surface layer Monin–Obukhov (Janjic) scheme
	Planetary boundary layer schemes	ACM2 (Pleim) PBL (ARW) (Pleim, 2007) Mellor-Yamada-Janjic TKE scheme (Janjic, 1994)
	Cumulus parameterization	Kain–Fritsch (new Eta) scheme (Kain, 2004)
EURAD-CTM	Method for calculation of photolysis frequencies	Tropospheric Ultra–Visible Model (Madronich, 1987)
	Cloud module	R2.6 version, based on Roselle and Binkowski (1999)
	Dry deposition module	Scheme from Zhang et al. (2003)
	Diffusion module	Bott (1989) algorithm
	Aerosol dynamics module (MADE)	MADE including APC and HDMR (Nieradzik, 2005)
	Kinetic chemistry mechanism	RACM–MIM mechanism (Geiger et al., 2003)
	Chemistry solver	Rosenbrock integrator with 2 stages (Verwer et al., 1999)

#### Table 1. Summary of the WRF model physic options used



The activity sectors of energy production and industrial combustion (SNAP 1 and 3) are the ones that most contribute to  $SO_2$  emissions, giving also an important contribution to  $NO_X$  emissions. Nevertheless, the transport sector (SNAP 7) is the main responsible for  $NO_X$  total emissions in Portugal. Domestic and industrial combustion and processes (SNAP 2, 3 and 4) emit mainly NMVOC, PM<sub>2.5</sub> and PM<sub>10</sub>. For NMVOC, the major emission source is the use of solvents (SNAP 6).

The analysis of the differences between total emissions projected for 2020 and estimated for 2012 (Figure 3b) shows that emissions tend to decrease for the majority of pollutants and activity sectors. This global decrease is, in some cases, a result of different sign/trend for different sectors. For example, the high reduction rate of NO<sub>X</sub> predicted for some sectors (namely SNAP 8 and 9) are balanced with the increase of others (e.g. SNAP2-residential combustion) resulting in a small percentage of the emission total reduction of this pollutant. An increase of SO<sub>2</sub>, NMVOC, PM<sub>2.5</sub> and PM<sub>10</sub> emissions from energy production (SNAP 1) is foreseen according to 2020 projections. This sector covers the large power plants and petroleum refineries. A slight increase of PM<sub>10</sub> emissions from SNAP4 is also verified.

In order to get the emission input data for modeling simulation, the emission totals were spatially disaggregated over the gridded simulation domain of 5x5 km<sup>2</sup> horizontal resolution (domain PT5, Figure 1). For area emission sources, namely SNAP sectors 2 to 10, the total emissions for 2012 and for 2020, by activity sector and by pollutant, were disaggregated according to the spatial distribution per municipality of the most recent national emission inventory available. Regarding the emissions

disaggregation of SNAP 2, 3, 6 and 9 for 2020 an additional disaggregation factor was considered – demographic projections per NUTIII regions for 2020, Figure 4 presents the NO<sub>X</sub>,  $PM_{10}$ ,  $PM_{2.5}$  and  $SO_2$  emissions in tonnes per grid cell, obtained for 2012 and 2020.

For SNAP 1 (point sources associated to energy production) the emissions for 2012 were based on the national emission inventory referred above and on the data reported to the European Commission in the scope of the large combustion plants directive (EIONET, 2014). For 2020, the emission totals for SNAP 1, considering the projections share of petroleum refineries and power plants by type of fuel, were distributed to the industrial plants following the proportions verified in 2012. The emissions resulting allocation is presented in Figure 4. The results highlight the increase of SO<sub>2</sub>, PM<sub>2.5</sub> and PM<sub>10</sub> emissions and the reduction of NO<sub>x</sub> emissions in some point sources, in agreement with the analysis of Figure 2b. For the modeling application, the point source emissions were allocated to the grid cell corresponding to the location of each industrial facility mapped in Figure 5.

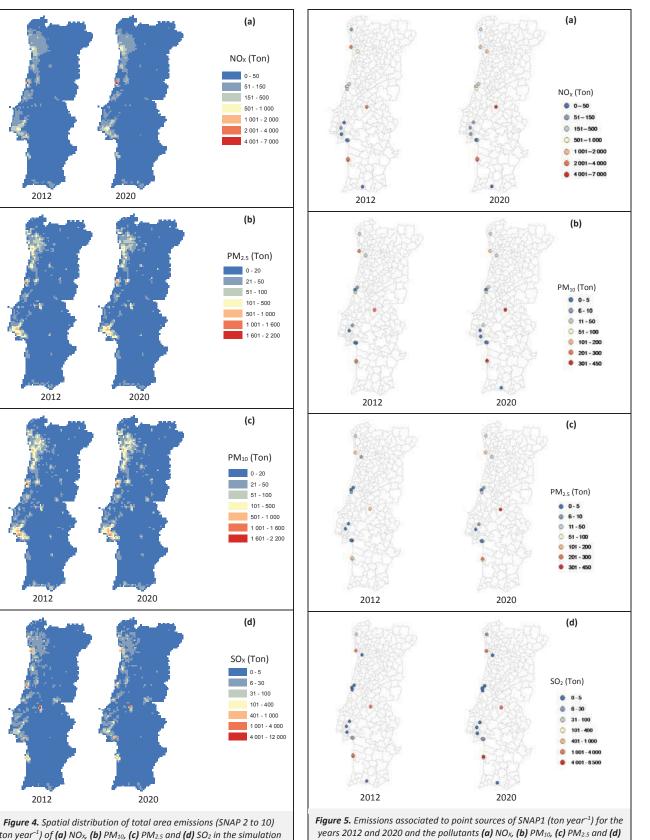
For the coarse domains (C125 and IP25) emissions from EMEP database were used (CEIP, 2014) for the year 2012 simulation and were kept unchanged for 2020. Thus, emissions changes outside Portugal for 2020 were not considered. Besides its importance to PM<sub>10</sub> concentrations (Monteiro et al., 2015), natural dust emissions from (Sahara) desert regions were not also considered in the scope of this study since there are no predictions of dust emissions for future scenarios.

2012

2012

2012

2012



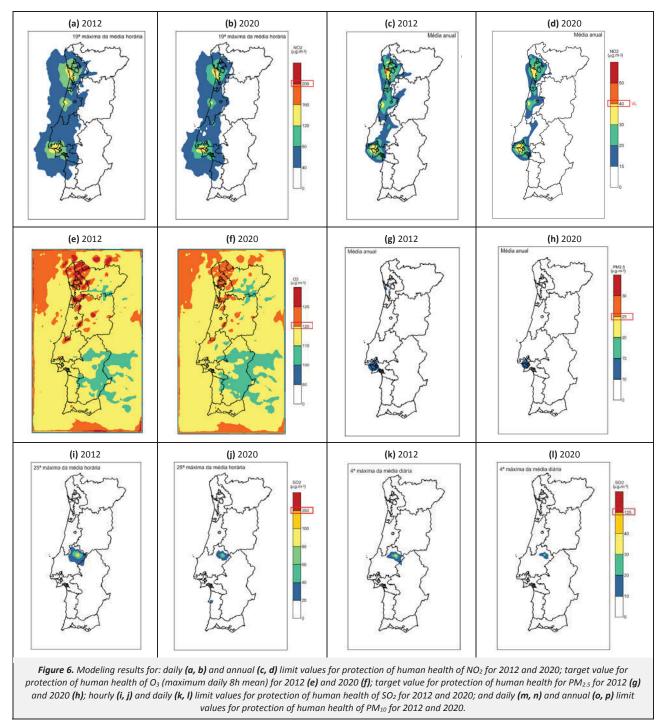
SO2.

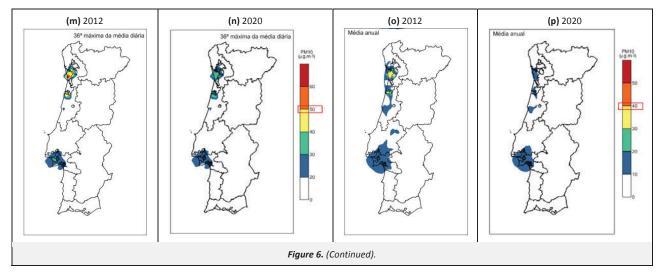
(ton year<sup>-1</sup>) of (a) NO<sub>X</sub>, (b)  $PM_{10}$ , (c)  $PM_{2.5}$  and (d)  $SO_2$  in the simulation domain grid.

### 4. Air Quality over Portugal for the Year 2020

The analysis of the modeling results will allow concluding about the impact of the national emission scenarios for 2020 on the air quality of Portugal. The previous evaluation/validation exercises performed for this modeling system were fundamental to support and guarantee the analysis of these model results. In several previous works (Monteiro et al., 2013a; Monteiro et al., 2013b) the EURAD modeling results were compared with observations from the air quality monitoring stations, for the several air pollutants and for a long period (one year) and also inter–compared with other air quality models. The results point out a very good correspondence between simulated and observed values for the various species, with a RMSE is, in average, below  $20 \ \mu g \ m^{-3}$ ; BIAS below  $-10 \ \mu g \ m^{-3}$  for the different pollutants (namely O<sub>3</sub>, NO<sub>X</sub> and PM<sub>10</sub>) and the correlation coefficient, in average, above 0.7 for O<sub>3</sub> and above 0.6 for PM<sub>10</sub> and NO<sub>X</sub>. These parameters give an estimation of the uncertainty associated with the model results, essential for a correct interpretation and analysis of the results.

Figure 6 presents the comparison between the 2012 and 2020 cases, according to the legislation parameters defined by Directive 2008/50/EC, for each of the main atmospheric pollutants, namely for NO<sub>2</sub>, SO<sub>2</sub>, PM<sub>10</sub> and PM<sub>2.5</sub>, and also for O<sub>3</sub>, a secondary pollutant produced apart from NO<sub>x</sub> and NMVOC precursors, with particular critical levels registered in Portugal (Monteiro et al., 2007; Monteiro et al., 2012).





Regarding the NO<sub>2</sub> (Figures 6a–6d) the modeling results indicate that there will be no significant changes foreseen in 2020. Only a small reduction (about 15%, around 6–7  $\mu$ g m<sup>-3</sup> in annual average) is predicted in the Porto urban area. These results reflect the small reduction expected in the total NO<sub>2</sub> emission values (around 18%; see comments on Figure 3).

The surface maps for O<sub>3</sub> (Figures 6e–6f) show similar patterns for 2012 and 2020 scenario, which mean that the exceedances of the target value modeled for 2012 year continue to occurred in 2020. For this case, additional measures would be needed to mitigate this pollutant concentration. A more detailed study regarding both precursor pollutants – NO<sub>X</sub> and VOC – is required in order to study the type of measures/strategies that would be more efficient to reduce O<sub>3</sub> values taking into account the interaction and chemistry processes involved (Seinfeld and Pandis, 2006).

In opposite to the previous pollutants, significant reduction is expected for  $SO_2$  concentrations (Figures 6i–6l), namely for the region where high values of this pollutant were estimated around an industrial point source (paper/pulp and cement industries), which is directly justified by the predicted emission reduction for 2020.

Regarding particulate matter, a reduction is foreseen for both daily and annual values of  $PM_{10}$  for 2020 scenario (Figures 6m–6p). This decrease is more evident in the urban areas of Porto and Lisbon, where this pollutant register the highest concentration values. It should be noticed that this reduction will allow fulfilling the legislation thresholds that were not accomplished in 2012. For  $PM_{2.5}$  (Figures 6g–6h) there are no expected changes regarding the annual average between 2012 and 2020.

In order to analyze more easily and identify the legislation compliance for all the different pollutants, the same surface concentration maps for 2020 are represented in Figure 7 but categorized according to the legislation fulfillment, namely "compliance unlikely"; "compliance uncertain" and "compliance likely".

This figure allows verifying easily that the legislation compliance for 2020 is expected to be in risk only for the NO<sub>2</sub> and O<sub>3</sub>. The compliance for NO<sub>2</sub> is uncertain for the two main urban areas (Porto and Lisbon). In the case of O<sub>3</sub>, the legislation

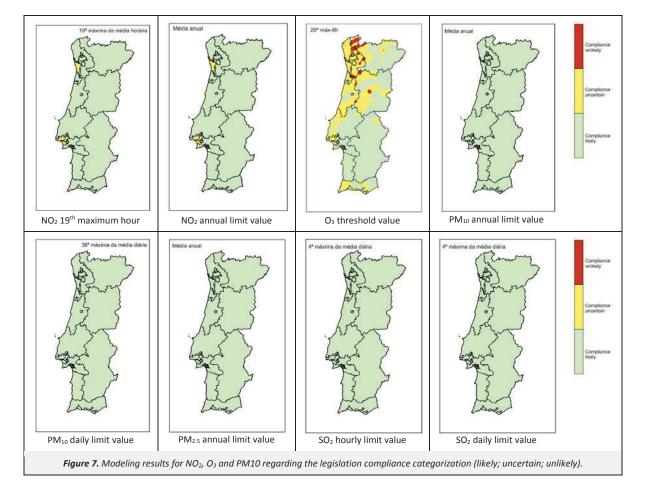
compliance is even "unlikely" for specific areas in the North and Central of Portugal and uncertain for a large region over the Northwest region. Reaching compliance in such specific and different locations requires further action on each precursor pollution sources, namely studying/investigating the NO<sub>X</sub>/VOC regime that indicates witch precursor controls the O<sub>3</sub> concentration (Pusede and Cohen, 2012). In cases of NO<sub>X</sub> limited regime, it will be recommended to act over the road transport sector, like restriction of heavy goods vehicles in urban centers and implementation of alternative traffic systems with differentiated road tolls; Low Emission Zones or even cut–off streets to traffic. In the cases of VOC regime, measures should focus on the use of solvents and specific industrial processes containing organic compounds. For PM and SO<sub>2</sub> the 2020 NEC scenario is very positive, where "compliance likely" is expected for all Portugal.

These results will be particular important to define the next Air Quality strategy for near future (2020–2030) that are being designed in order to improve and solve current situations of non compliance of air quality legislation.

#### 5. Summary and Conclusions

In order to evaluate the impact on air quality of the NEC scenarios, numerical simulations were performed with the WRF–EURAD modeling system, for the current situation (2012) and 2020 year, using the same (2012) meteorological conditions as input. The results were analyzed for the most critical atmospheric pollutants, namely NO<sub>2</sub>, O<sub>3</sub>, SO<sub>2</sub>, and particulate matter ( $PM_{10}$  and  $PM_{2.5}$ ), taking as guide the legislation limit values and its fulfillment.

The differences between both emissions scenarios indicate a trend to decrease for the majority of pollutants and activity sectors, besides high increase rates are foreseen for 2020 projections for some specific sectors, like energy production (SNAP 1), industrial processes for  $PM_{10}$  and residential combustion for NO<sub>x</sub>. The modeling results confirm the efficiency of the emissions reduction strategies defined by the NEC program for 2020, in particular for particulate matter and SO<sub>2</sub>, but do not solve the non–compliance regarding the O<sub>3</sub> threshold value for protection of human health. Additional strategic mitigation actions need to be designed/developed, with focus on ozone and its precursors, at local and regional scale.



#### Acknowledgments

The authors acknowledge the financial support of the Portuguese Agency for Environment, and also FCT for the Ph.D grants of I. Ribeiro (SFRH/BD/60370/2009), A. Fernandes (SFRH/ BD/86307/2012) and C. Gama (SFRH/BD/87468/2012), and the post–doc grants of A. Monteiro (SFRH/BPD/63796/2009) and J. Ferreira (SFRH/BPD/40620/2007) and H. Martins (SFRH/BPD/6874/2009). The authors would like to acknowledge the financial support of FEDER through the COMPETE Programme and the national funds from FCT – Science and Technology Portuguese Foundation – within project PEst–C/MAR/LA0017/2013 for the MAPLIA Project (PTDC/AAG–MAA/4077/2012) and CLICURB project (EXCL/AAG–MAA/0383/2012).

#### References

- APA (Portuguese Environmental Agency), 2014. National Strategy for Air, Synthesis Report, ENAR 2014–2020.
- Arakawa, A., Lamb, V.R., 1977. Computational design of the basic dynamical processes of UCLA general circulation model, in *General Circulation Models of the Atmosphere*, edited by Chang, J., Academic Press, London, pp. 173–265.
- Aquilina, N., Dudek, A.V., Carvalho, A., Borrego, C., Nordeng, T.E., 2005. MM5 high resolution simulations over Lisbon. *Geophysical Research Abstracts* 7, art. no. 08685.
- Borrego, C., Monteiro, A., Pay, M.T., Ribeiro, I., Miranda, A.I., Basart, S., Baldasano, J.M., 2011. How bias–correction can improve air quality forecasts over Portugal. *Atmospheric Environment* 45, 6629–6641.
- Bott, A., 1989. A positive definite advection scheme obtained by nonlinear renormalization of the advective fluxes. *Monthly Weather Review* 117, 1006–1016.

- Carvalho, A.C., Carvalho, A., Gelpi, I., Barreiro, M., Borrego, C., Miranda, A.I., Perez–Munuzuri, V., 2006. Influence of topography and land use on pollutants dispersion in the Atlantic coast of Iberian Peninsula. *Atmospheric Environment* 40, 3969–3982.
- CEIP, 2014: http://www.ceip.at/ms/ ceip\_home1/ceip\_home/webdab\_ emepdatabase accessed in July 2014.
- EEA, 2014. NEC Directive Status Report 2013, Reporting by Member States under Directive 2001/81/EC of the European Parliament and of the Council of 23 October 2001 on National Emission Ceilings for Certain Atmospheric Pollutants, EEA Technical Report No 10/2014.
- EEA, 2013a. Exposure of Ecosystems to Acidification, Eutrophication and Ozone (Indicator CSI 005), European Environment Agency.
- EEA, 2013b. Air Quality in Europe 2013 Report, EEA Report 9/2013. Copenhagen, Denmark, 107 pages.
- EEA, 2013c. Exceedance of Air Quality Limit Values in Urban Areas (Indicator CSI 004), European Environment Agency.
- EIONET, 2014: http://cdr.eionet.europa.eu/pt/eu/lcpes/, accessed in October 2014.
- Elbern, H., Strunk, A., Schmidt, H., Talagrand, O., 2007. Emission rate and chemical state estimation by 4–dimensional variational inversion. *Atmospheric Chemistry and Physics* 7, 3749–3769.
- Fernandez, J., Montavez, J.P., Saenz, J., Gonzalez–Rouco, J.F., Zorita, E., 2007. Sensitivity of the MM5 mesoscale model to physical parameterizations for regional climate studies: Annual cycle. *Journal of Geophysical Research–Atmospheres* 112, art. no. D04101.
- Geiger, H., Barnes, I., Bejan, I., Benter, T., Spittler, M., 2003. The tropospheric degradation of isoprene: An updated module for the regional atmospheric chemistry mechanism. *Atmospheric Environment* 37, 1503–1519.

- Hong, S.-Y., Lim, J.-O.J, 2006. The WRF single-moment 6-class microphysics scheme (WSM6). Journal of the Korean Meteorological Society 42, 129–151.
- IPCC (Intergovernmental Panel on Climate Change), 2014. Summary for Policymakers, in Climate Change 2014: Impacts, Adaptation, and Vulnerability. Part A: Global and Sectoral Aspects, Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, edited by Field, C.B., Barros, V.R., Dokken, D.J., Mach, K.J., Mastrandrea, M.D., Bilir, T.E., Chatterjee, M., Ebi, K.L., Estrada, Y.O., Genova, R.C., Girma, B., Kissel, E.S., Levy, A.N., MacCracken, S., Mastrandrea, P.R., White L.L., Cambridge University Press, Cambridge, United Kingdom and New York, USA, pp. 1–32.
- Janjic, Z.I., 1994. The step-mountain ETA coordinate model Further developments of the convection, viscous sublayer, and turbulence closure schemes. *Monthly Weather Review* 122, 927–945.
- Kain, J.S., 2004. The Kain–Fritsch convective parameterization: An update. Journal of Applied Meteorology 43, 170–181.
- Madronich, S., 1987. Photodissociation in the atmosphere .1. Actinic flux and the effects of ground reflections and clouds. *Journal of Geophysical Research–Atmospheres* 92, 9740–9752.
- Martinho Marta-Almeida, M., A. Rocha, J. Castanheira, P. Melo-Gonçalves.
  2014. High resolution climatic simulations in the Iberian Peninsula:
  Model validation. International Conference on Ecohydrology, Soil and
  Climate Change. EcoHCC14- 97, Sept. 2014, Tomar, Portugal, p.97.
- Martins, H., 2012. Urban compaction or dispersion? An air quality modelling study. Atmospheric Environment 54, 60–72.
- Monteiro, A., Fernandes, A.P., Gama, C., Borrego, C., Tchepel, O., 2015. Assessing the mineral dust from North Africa over Portugal region using BSC–DREAM8b model. Atmospheric Pollution Research 6, 70–81.
- Monteiro, A., Ribeiro, I., Tchepel, O., Carvalho, A., Martins, H., Sa, E., Ferreira, J., Martins, V., Galmarini, S., Miranda, A.I., Borrego, C., 2013a. Ensemble techniques to improve air quality assessment: Focus on O<sub>3</sub> and PM. *Environmental Modeling & Assessment* 18, 249–257.
- Monteiro, A., Ribeiro, I., Tchepel, O., Sá, E., Ferreira, J., Carvalho, A., Martins, V., Strunk, A., Galmarini, S., Elbern, H., Schaap, M., Builtjes, P., Miranda, A.I., Borrego, C., 2013b. Bias correction techniques to improve air quality ensemble predictions: Focus on O<sub>3</sub> and PM over Portugal. *Environmental Modeling & Assessment* 18, 533–546.
- Monteiro, A., Strunk, A., Carvalho, A., Tchepel, O., Miranda, A.I., Borrego, C., Saavedra, S., Rodriguez, A., Souto, J., Casares, J., Friese, E., Elbern, H., 2012. Investigating a high ozone episode in a rural mountain site. *Environmental Pollution* 162, 176–189.
- Monteiro, A., Miranda, A.I., Borrego, C., Vautard, R., 2007. Air quality assessment for Portugal. Science of the Total Environment 373, 22–31.
- NCEP/NOAA (National Centers for Environmental Prediction/National Oceanic and Atmospheric Administration), 2000. NCEP FNL Operational Model Global Tropospheric Analyses, Continuing from July 1999, Research Data Archive at the National Center for Atmospheric Research, Computational and Information Systems Laboratory.

- Nieradzik, L.P., 2011. Four–Dimensional Variational Assimilation of Aerosol Data from In–situ and Remote Sensing Platforms. Ph.D. Thesis, Universitat zu Koln.
- Nieradzik, L.P., 2005. Application of a High Dimensional Model Representation on the Atmospheric Aerosol Module MADE of the EURAD–CTM. Master Thesis, Institut fur Geophysik und Meteorologie der Universitat zu Koln.
- Pleim, J.E., 2007. A combined local and nonlocal closure model for the atmospheric boundary layer. Part II: Application and evaluation in a mesoscale meteorological model. *Journal of Applied Meteorology and Climatology* 46, 1396–1409.
- Pusede, S.E., Cohen, R.C., 2012. On the observed response of ozone to NOx and VOC reactivity reductions in San Joaquin Valley California 1995– present. Atmospheric Chemistry and Physics 12, 8323–8339.
- Ribeiro, I., Valente, J., Amorim, J., Miranda, A., Lopes, M., Borrego, C., Monteiro, A., 2014. Air quality modelling and its applications, in *Current Environmental Issues and Challenges SE – 3*, edited by Cao, G., Orru, R., Springer, Netherlands, pp. 45–56.
- Roselle, S., Binkowski, F., 1999. Capter 11: Cloud Dynamics and Chemistry, in Science Algorithms of the EPA Models–3 Community Multiscale Air Quality (CMAQ) Modeling System, EPA Report EPA/600/R–99/030.
- Seinfeld, J.H., Pandis, S.N., 2006. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 2<sup>nd</sup> edition, John Wiley & Sons, Inc., Hoboken, New Jersey, 1232 pages.
- Skamarock, W.C., Klemp, J.B., Dudhia, J., Gill, D.O., Barker, D.M., Huang, X.Y., Wang, W., Powers, J.G., 2008. A Description of the Advanced Research WRF Version 3, NCAR Technical Note, National Center for Atmospheric Research, Boulder, Colorado, USA.
- UNECE (United Nations Economic Commission for Europe), 2012a. Decision 2012/1 Amendment of Annex I to the 1999 Protocol to Abate Acidification, Eutrophication and Ground–level Ozone, http://www.unece.org/fileadmin/DAM/env/Irtap/full%20text/ECE\_EB. AIR\_111\_Add1\_1\_E.pdf, accessed in July 2014.
- UNECE (United Nations Economic Commission for Europe), 2012b. Decision 2012/2 Amendment of the text of and annexes II to IX to the 1999 Protocol to Abate Acidification, Eutrophication and Ground–level Ozone and the Addition of New Annexes X and XI (ECE/EB.AIR/111/ Add.1), http://www.unece.org/fileadmin/DAM/env/documents/2013/ air/ECE\_EB.AIR\_111\_Add.1\_\_ENG\_DECISION\_2.pdf, accessed in July 2014.
- Verwer, J.G., Spee, E.J., Blom, J.G., Hundsdorfer, W., 1999. A second–order Rosenbrock method applied to photochemical dispersion problems. *Siam Journal on Scientific Computing* 20, 1456–1480.
- Wang, W., Bruyere, C., Duda, D., Dudhia, J., Gill, D., Kavulich, M., Keene, K., Chuan, H.–C., Michalakes, J., Rizvi, S., Zhang, X., 2014. WRF–ARW Version 3 Modeling System User's Guide.
- Zhang, L., Brook, J.R., Vet, R., 2003. A revised parameterization for gaseous dry deposition in air–quality models. *Atmospheric Chemistry and Physics* 3, 2067–2082.