

Extended summary

# Tropospheric ozone behavior as a function of precursor emissions

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Abstract. Air quality monitoring stations placed in Marche Region, over the last decade, measured high concentrations of tropospheric ozone. The aim of this work is to analyze the formation of this pollutant, particularly in the Area at High Risk of Environmental Crisis (AERCA). Network of air monitoring stations, emission inventories and dispersion models are useful tools and they should be used together. The monitoring stations collect data at fixed points. Emission inventories and environmental models are closely related: a detailed inventory is required by each model; at the same time, the use of models is recommended to update and validate an inventory. The implementation of the modelling system RAMS-EPS3-CAMx-OSAT was required to evaluate the chemical ozone formation and destruction, and corrective factors can be applied to the emissions inventory in order to harmonize the results with data obtained by monitoring stations. The photochemical model, like CAMx (Comprehensive Air quality Model with eXtensions), considers secondary pollutants arising from chemical reactions in the atmosphere; CAMx is an Eulerian photochemical dispersion model that allows the assessment of gaseous and particulate air pollution over many scales ranging from sub-urban to continental. The OSAT tool (Ozone Source Apportionment Technology) allows CAMx to track source-region and source-category contributions to the predicted ozone concentrations. Thus, for any selected receptor and for any selected period, the model gives information about the likely distribution of ozone and ozone precursors by source category and by source region. Similarly, it assesses whether the ozone at the selected time and location would more likely respond to upwind NO<sub>x</sub> or VOC controls. In



addition, it was possible to analyse the ozone behaviour in diverse areas referring to land use (e.g. Road, Country, Industrial Area, Etc.). Information about the contribution of the different types of source emission and sectors allowed us to develop a tentative best ozone-control strategy to lower ozone peaks and to avoid ozone episodes.

Keywords. air pollution, tropospheric ozone, CAMx, OSAT, air control strategies

#### 1 Problem statement and objectives

This work presents a rather complex set of simulations carried out to better describe the ozone behavior in the Marche Region especially in a particular area located across the Adriatic Sea, under the AERCA restraint. The risk is mainly due to the concurrent presence of a big oil refinery, several highways, the local airport, and a rather big port, including industrial harbors. This situation led to high levels of several different species of pollutants, in the past (especially Volatile Organic Compounds), many of whom deeply affect ozone cycles. In previous years, comparatively high concentrations of ozone were registered by monitoring stations, also in other places of Marche Region.

The entire "Ozone Problem" in such area was modeled by the means of the photochemical model CAMx (Comprehensive Air quality Model with eXtensions) with the additional implementation of a dedicated probing tool called OSAT (Ozone Source Apportionment Technology) specially developed for the study of the ozone dynamics.

The results provided us with important information about the conditions of ozone formation, the role of each single emission group, and, more specifically, information about when and where a certain pollutant involved in the ozone dynamics was released.

#### 1.1 Human health effects and climate interactions

Ozone is continually produced and destroyed in the atmosphere by chemical reactions. The respiratory system is the primary target of the ozone oxidizing effects on human health. Exposure to elevated concentrations is associated with increased hospital admissions for pneumonia, chronic obstructive pulmonary disease, asthma, allergic rhinitis and other respiratory diseases [1]. The extent of adverse respiratory consequences due to ground-level ozone depends on a number of factors, including pollutant concentrations, duration of exposure, local climate, individual sensitivity, and any preexistent respiratory disease. The Air Quality Standards in Italy, according to Europe, define the maximum daily eight hour mean of 120  $\mu$ g/m<sup>3</sup>, and the information threshold of 180  $\mu$ g/m<sup>3</sup> during one hour [2].

Tropospheric ozone is also a greenhouse gas: after carbon dioxide and methane, it is the third most important contributor to greenhouse radiative forcing [3]. Since pre-industrial times, the radiative forcing value due to tropospheric ozone is estimated to be +0.35 W m<sup>-2</sup> (range 0.25-0.65).

## 2 Ozone formation in the troposphere

#### 2.1 VOC/NO<sub>X</sub> role

Tropospheric ozone is produced by photochemical oxidation of carbon monoxide (CO), methane (CH<sub>4</sub>) and non-methane volatile organic compounds (VOC) in the presence of  $NO_x$ . The hydroxyl radical (OH) is the key reactive species in the chemistry of ozone formation, and it can react with CO, CH<sub>4</sub> and VOC. In general, methane is not simulated explicitly in ozone models. The sensitivity of ozone formation to VOC and  $NO_x$  at any given time is attributable to the fate of radicals, and the production does not increase linearly with an increase in the precursors concentrations. In general, increasing VOC concentrations



tions means more ozone, increasing  $NO_x$  may lead to either more or less ozone depending on the prevailing VOC-to- $NO_x$  ratio [4].

The radical pool is often referred to as odd hydrogen  $(HO_x)$  and is most usefully considered as the sum of OH,  $HO_2$  and  $RO_2$  radicals. Ozone formation occurs through the following sequence of reactions. The sequence is usually initiated by the reaction of various CO or VOC with the OH radical according to formulae (1) and (2).

$$CO + OH \xrightarrow{+O_2} CO_2 + HO_2 \tag{1}$$

$$RH + OH \xrightarrow{+O_2} RO_2 + H_2O$$
(2)

This is followed by the conversion of NO to NO<sub>2</sub> through reaction with HO<sub>2</sub> or RO<sub>2</sub> radicals, which also regenerates OH according to formulae (3) and (4). RO<sub>2</sub> represents any of a number of chains of organics with an O<sub>2</sub> attached

$$\mathrm{HO}_2 + \mathrm{NO} \to \mathrm{NO}_2 + \mathrm{OH} \tag{3}$$

$$RO_2 + NO \xrightarrow{+O_2} R'CHO + HO_2 + NO_2$$
(4)

 $NO_2$  is photolyzed to generate atomic oxygen, which combines with  $O_2$  to create  $O_3$  through reaction (5) and (6).

$$NO_2 + hv \to NO + 0 \tag{5}$$

$$\mathbf{0} + \mathbf{0}_2 + \mathbf{M} \to \mathbf{0}_3 + \mathbf{M} \tag{6}$$

Ozone episodes in polluted regions are usually due to the ozone production sequence shown above. However, at nighttime and in the immediate vicinity of very large emissions of NO, ozone concentrations are depressed through the process of  $NO_x$  titration, according to the formula (7).

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{7}$$

There is a competition between VOC and  $NO_x$  for the OH radical. At a high ratio of VOC to  $NO_x$  concentration, OH will react mainly with VOC while, at a low ratio, the  $NO_x$  reaction can predominate [4].

When the VOC/NO<sub>x</sub> concentration ratio is approximately 5.5:1, with the VOC concentration expressed on a carbon atom basis, the rates of reaction of VOC and NO<sub>x</sub> with OH are equal. Whenever the VOC/NO<sub>x</sub> ratio is lower than 5.5:1, reaction of OH with NO<sub>2</sub> predominates over reaction of OH with VOC. The OH-NO<sub>2</sub> reaction (8) removes OH radicals from the active VOC oxidation cycle, retarding the further production of O<sub>3</sub>.

$$OH + NO_2 + M \to HNO_3 + M \tag{8}$$

Under these conditions, called VOC-limited, a decrease in  $NO_x$  emissions favors  $O_3$  formation. Conversely, when the ratio exceeds 5.5:1, OH reacts preferentially with VOC. At very low  $NO_x$  concentration, reaction (9) becomes significant and it removes free radicals from the system.

$$\mathrm{HO}_2 + \mathrm{HO}_2 \to \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2 \tag{9}$$

This condition is named  $NO_x$ -limited, because the growth of  $NO_x$  emissions induces the reaction (3) and consequently the ozone formation.



#### 2.2 Sillman Indicator

In reality, many of the trajectories start out VOC-limited and become  $NO_x$ -limited during the course of the day essentially because the  $NO_x$  is depleted more rapidly than the VOC. Nitric acid (HNO<sub>3</sub>) production, according to the reaction (8), is indicative of plentiful  $NO_x$  while peroxide formation (H<sub>2</sub>O<sub>2</sub>) is indicative of scarce  $NO_x$ .

Sillman (1995) has exploited this situation to develop useful indicators of VOC vs.  $NO_{x-1}$  limited ozone formation based on the ratio of peroxide production to nitric acid production [5]. Sillman proposed that the transition between these conditions occurs when:

$$P_{H_2O_2}/P_{HNO_3} = 0.35 \tag{10}$$

Before midday, with an initial VOC/NO<sub>x</sub> ratio 10:1, the Sillman ratio is less than 0.35 indicating VOC-limited ozone formation. After that, it exceeds 0.35 indicating NO<sub>x</sub>-limited ozone formation. After sunset, the ratio falls below 0.35 again, but this is after the ozone peak and the concepts of VOC and NO<sub>x</sub>-limitation are no longer relevant [6].

The true impact of VOC is related more closely to the reactivity of the VOC species with respect to OH rather than to the total amount of VOC. Locations with highly reactive VOC, e.g. xylenes or isoprene, are more likely to have  $NO_x$ -limited chemistry than locations with similar total VOC but lower reactivity [7]. For this reason the photochemical models require the chemical speciation of the emission inventory.

## 3 Ozone modeling system

#### 3.1 Meteorological model

A coastal region is influenced by many meteorological phenomena due to the interactions between breezes and large-scale wind systems. Mesoscale air flows in coastal regions are mainly determined by land-sea temperature contrast that drives land-sea breezes, and by the orography that drives mountain-valley breezes while the shape of the coastline has an effect on mesoscale wind flow [8]. A mesoscale meteorological model (RAMS) has been used. RAMS is a versatile modelling system capable of simulating flows from the scale of a global hemisphere to the scale of a building [9] with numerous options including multiple nesting, and several convective and boundary layer parameterization options.

## 3.2 Emission inventory model

A photochemical model simulates the hour-by-hour photochemistry occurring for each grid cell in the modeling domain; consequently, the input emissions data must contain a comparable level of resolution. Total emissions (e.g., VOC,  $NO_x$ ) must be chemically allocated into the chemical classes employed by the model. Additionally, the emissions data must be spatially allocated by grid cell for each hour of the modeling episode [10]. The flexibility of EPS3 (*Emissions Processing System*, version 3.20) provides the user with many options for processing their emissions inventory. EPS3 consists of a series of Fortran modules that perform these intensive data manipulations, producing an emissions inventory for photochemical modeling. Referring to ozone assessment, the model is usually applied for a multi-day period during which adverse meteorological conditions result in elevated concentrations. For the present study, we used three differed grids: one master grid and two nested grids. The coarse grid (G1), as shown in Figure 1a, is 960x800 km wide and covers most



of continental Italy through its 60x50 cells with 16km step. The second nested grid (G2) is 232x219 Km wide, well covers the Marche region, and is made of 58x54 cells of 4 km steps. The finest grid (G3) is 50x50 km wide and is made of 50x50 cells of 1 km steps. It covers the AERCA restraint (Fig. 1b).



Figure 1. Master grid G1 and nested grid G2 (a); grid G3 (b) with Area at High Risk of Environmental Crisis (red)

The air emission inventories here in use has been derived from the EMEP Centre on Emission Inventories and Projections [11] for the sources outside Italy, the Italian Emission Inventory 2005 [12] for all the provinces outside Marche Region, and the Emission Inventory [13] to the municipality level of Marche Region.

## 3.3 Photochemical model

CAMx (Comprehensive Air quality Model with eXtensions) is an Eulerian photochemical dispersion model that allows an integrated "one-atmosphere" assessment of gaseous and particulate air pollution (ozone, PM2.5, PM10, air toxics, mercury) over many scales ranging from sub-urban to continental.

CAMx simulates the emission, dispersion, chemical reaction, and removal of pollutants in the troposphere by solving the pollutant continuity equation for each chemical species on a system of nested three-dimensional grids [6]. The Eulerian continuity equation describes the time dependency of the average species concentration within each grid-cell volume as a sum of all of the physical and chemical processes operating on that volume.

## 3.4 Source apportionment tool

Ozone source apportionment (OSAT), in CAMx, tracks the contributions to each grid cell from emissions source groups, emissions source regions, initial conditions, and boundary conditions with reactive tracer species ( $NO_x$ , VOC, and  $O_3$ ). Tracers provide information on the relative importance of transport and chemistry [14]. To distinguish VOC and  $NO_x$ -limited regimes, the tool uses the Sillman's indicator. The tracers operate as spectators to the normal CAMx calculations so that the underlying CAMx predicted relationships between emission groups (sources) and ozone concentrations at specific locations (receptors)



are not perturbed [6]. The emission data was roughly split into three different groups: *Industrial* (*I*: anthropogenic fixed point sources; from SNAP97 sector 1 to 6, and 9), *Transport* (*T*: road transport and other mobile sources; SNAP97 sectors 7 and 8) and *Natural* (*N*: agriculture, forest and other natural sources; SNAP97 sectors 10 and 11).

The tool OSAT needs an input file called Source Map file that allows the user to indicate other subdomains of emission within the grid set before. A Source Map file is required for the master grid and optional for the nested ones. The Source Map, showed in Figure 2, was designed according to the borders of Italian Regions. Smaller Regions were joined together.



Figure 2. Source Map file, each number represents a Region. The map of Italy is used only to distinguish the regional boundaries, but there isn't in the Source Map file

## 4 Operational evaluation results

#### 4.1 Base case

Our study was performed over four days, namely from August 25 to August 28 of 2006.

The chemistry mechanisms activated was Carbon Bond IV [15] with 113 reactions and up to 76 species (up to 44 state gases, up to 22 state particulates and 10 radicals).

The results of first simulation are shown in Figure 3-4. The emission scenario is the base case, without any modification to the emission inventories. The boundary conditions, namely the primary and secondary pollutants released outside the grid G1, are evaluated from EMEP prescribed values [16].

The predicted concentrations are in agreement with measurements of the two monitoring stations placed in AERCA: "Chiaravalle/2" (Fig. 3) and "Falconara Scuola" (not reported). The differences are larger in the first two days of simulation, then become smaller. The model needs at least two days of simulation to give acceptable results simply due to the self-tuning: derived from initial and boundary concentrations ozone has less weight percentage after the first two days. In Figure 4, the hourly amount of ozone formed is reported with respect to the condition of formation for all emission groups and all emission areas of August 28. It distinguishes between NO<sub>x</sub>-limited (O3N) and VOC-limited (O3V). The



initial and boundary tracers are ozone not chemically produced; this is released during the first hour of simulation or, continuously, in the lateral boundaries, respectively.



Figure 3. Results with EMEP boundary concentrations at "Chiaravalle/2" monitoring station



Figure 4. Source apportionment applied to "Falconara Scuola" monitoring station

During the first part of the morning, at high concentration of  $NO_x$ , the reaction of the radical  $HO_x$  is faster with  $NO_x$  than with VOC and so the production of nitric acid, according to Formula (8), is high. The Sillman Indicator is below the transition point (VOC-limited situation) up to about 12:30 PM. At this point, because of a low concentration of  $NO_x$ , the radical  $HO_x$  reacts faster with VOC, the radical-radical reaction (9) becomes predominant and the Sillman indicator starts increasing ( $NO_x$ -limited situation). The tracers in Figure 4 match this behavior. A detailed analysis carried out on the Area at High Risk of Environmental Crisis inside the finest grid (G3) has showed a more efficient ozone depletion, after sunset, over the main highway, an area where NO emissions are very high (removal of ozone via reaction (7) is favored).

## 4.2 Ozone control stategies

Information about ozone condition of formation could be very useful in tuning ozone control strategies to reach acceptable air quality and to avoid ozone episodes. Generally, rural areas appear to be predominantly  $NO_x$ -limited: in this regime, an increase in  $NO_x$  concentrations is always associated with increased ozone production. Conversely, in a VOClimited situation, reducing the  $NO_x$  emission will result in an increased ozone concentra-



tion since less  $NO_2$  will be available to reaction (8), then just a small amount will be transformed into  $HNO_3$ . So, the rate of ozone formation is controlled by reactions (3) and (4) and increases with increasing VOC and decreases with increasing  $NO_x$ . Several further simulations through speculative reductions of emission were carried out to investigate how alterations in emission scenarios would influence ozone behavior in the area.



Figure 5. Ozone response to new emission scenarios, at "Falconara Scuola" site



Figure 6. Ozone tracer O3V (formation under VOC-limited conditions) response to new emission scenarios, at "Falconara Scuola" site



Figure 7. Ozone tracer O3N (formation under NO<sub>x</sub>-limited conditions) response to new emission scenarios, at "Falconara Scuola" site



Figures 5-7 show the ozone response in two different scenarios with 40% reduction of NO<sub>x</sub> or of VOC in emissions inventory. As we can see, a 40% reduction of VOC emissions will result in lower ozone concentrations, while reduced NO<sub>x</sub> emissions, will trigger an increase of the ozone concentration.

In the simulation with 40% reduction of  $NO_x$  emissions, the  $NO_x$ -limited situation happens before the one predicted by base case (Fig. 7) because of the different VOC/NO<sub>x</sub> ratio given in input to the model. The higher this ratio is, the earlier the transition occurs.

The ozone behavior should be matched with the  $VOC/NO_x$  ratio, including that measured at "Falconara Scuola" monitoring station (Fig. 8).



Figure 8.  $VOC/NO_X$  measured at "Falconara Scuola" monitoring station (black), and the ratio simulated by CAMx in three different emission scenarios

The monitored VOC/NO<sub>x</sub> ratio is always above the transition point (VOC/NO<sub>x</sub>>5.5), thus ozone formation is NO<sub>x</sub>-limited. Conversely, CAMx model simulated a VOC-limited situation in the first part of the morning followed, after midday, by a NO<sub>x</sub>-limited situation. Emission rates are probably the largest source of uncertainty in NO<sub>x</sub> and VOC predictions. Figure 9 shows the NO<sub>x</sub> monitored and predicted at "Falconara Scuola" station in the base case scenario: the values are similar.



Figure 9. NO and  $NO_2$  simulated by CAMx in base case emission scenario, and  $NO_2$  measured at "Falconara Scuola" monitoring station (green)



The differences between the predicted and measured  $VOC/NO_x$  ratio arise from hydrocarbons. In fact, the uncertainty associated with emission of biogenic and anthropogenic hydrocarbons are high [7].

#### 4.3 Sensitivity to emission inventories

Several scenarios were tested, using the data obtained from previous simulations, to better fit model results to measurements. In all of these, multiplicative factors to hydrocarbons emissions of Marche Region were applied.

Figures 10-11 show the predicted hydrocarbons and ozone for the modified scenario (a factor of five to VOC emissions was applied) in all the simulating period.



Figure 10. Monitored VOC at "Falconara Scuola" site and VOC predicted for two emission scenarios: base case and that with a factor of five to VOC emissions of Marche Region



Figure 11. Results with new emission scenario at "Falconara Scuola" monitoring station

#### 5 Discussion and conclusions

Results from base and modified emission scenarios are showed. The modeling system RAMS-EPS3-CAMx-OSAT well simulates the behavior of ozone in many places of Marche Region.

The emission inventories are often the largest source of uncertainty in model predictions. Ozone precursor sensitivity depends critically on emission rates for anthropogenic VOC



and  $NO_x$ , on the speciation of anthropogenic VOC, and on emission rates for biogenic VOC. Moreover, biogenic hydrocarbons usually are highly reactive.

Control strategies establish that ozone concentrations are difficult to predict if there are not reliable data on emissions and concentrations of ozone precursors.

Based on such evidence, policy makers must be aware that stopping industrial activities and/or private cars, with the aim of reducing ozone levels, may lead to exacerbation of phenomena and even to ozone episodes. In fact, reducing such human activities may lead to a further increase of VOC/NO<sub>x</sub> ratio since most VOC are due to diffuse emissions while NO<sub>x</sub> are mostly stack and exhaust-pipe emissions.

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