



Wildfires impact on surface nitrogen oxides and ozone in Central Italy

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ABSTRACT

A summer campaign in Central Italy was carried out to study the impact of fire emissions on the mixing ratios of surface trace gases. Observations with a selective and sensitive instrument that uses the laser induced fluorescence technique for direct measurements of nitrogen dioxide (NO₂), show a significant increase of NO₂ mixing ratios, in the evening, when a fire plume reached the observations site. The increase of NO₂ mixing ratios is well correlated ($R=0.83$) with that of particulate matter (PM), which is one of the primary product of forest and grassland fires. The tight correlation between NO₂ and PM is used to improve the performance of a statistical regression model to simulate the observed O₃, and to highlight the effect of fire emissions on the O₃ mixing ratios. The statistical regression model of O₃ improves in terms of performance (bias reduction of 77% and agreement enhancement of 10% for slope and correlation coefficient) when PM_{2.5} is included as additional input and proxy of the fire emissions among the usual input parameters (meteorological data and NO₂ mixing ratios). A case study, comparing observed and modeled O₃ in different days (with and without fire plume), suggests an impact of fire emissions on the O₃ mixing ratios of about 10%.

Keywords: Nitrogen dioxide, ozone, biomass burning, urban pollution, laser induced fluorescence



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1. Introduction

Ozone (O₃) together with aerosols is a tropospheric pollutant and greenhouse gas (IPCC, 2013). In atmosphere, O₃ is produced by the photolysis of nitrogen dioxide (NO₂), which in turn is the result of the oxidation of volatile organic compounds (VOCs) in presence of nitrogen oxide (NO). O₃ production is a non-linear function of the NO_x (NO+NO₂) concentrations (Kleinman, 2005), for this reason, the accurate measurement of NO_x is central to study the O₃ evolution. Combustion processes are the main sources of NO_x but their emissions from fires have still large uncertainties (Jaegle et al., 2005). The transport and removal of NO_x are controlled by reactive nitrogen compounds (NO_y), which are the sum of all the reservoir species of NO_x (NO_y=NO+NO₂+RO₂NO₂+RONO₂+HNO₃+2xN₂O₅+HONO+other nitrates). These species are produced in proximity of NO_x sources and their concentrations may be highly influenced by fire emissions (Bertram et al., 2005). Peroxyacyl nitrate (PAN) is produced by the oxidation of VOCs in presence of NO₂ and it has a lifetime on the order of days. PAN long lifetime allows long distance (thousands of kilometers) transport and, once dissociated, alters the levels of NO_x and ozone, even in areas not impacted by the fire (Val Martin et al., 2008).

Biomass burning produces primarily water vapor, carbon dioxide (CO₂) and carbon monoxide (CO). At the same time, in these combustion processes methane (CH₄), a variety of VOCs and carbon aerosols are emitted and, therefore released into the atmosphere. On global scale, fire emissions are one of the main sources of some of the species above, like CO and carbon aerosols

(Andreae and Merlet, 2001; Page et al., 2002). All the emissions from fires (burning of biomass in open air) are controlled by simple, but very variable, factors e.g. the quantity of water involved in the plant combustion, their size and the wind conditions. All these factors determine the overall efficiency of the combustion, which is defined as the fraction of emitted CO₂ compared to the total amount of carbon in the plant. Since these combustion processes are not 100% efficient, there is not complete conversion of all the plant carbon into CO₂. Because of this inefficient combustion, there is a significant emission of VOCs and aerosols. The VOCs released into the atmosphere are mainly oxidized by hydroxyl radical (OH) and nitrate radical (NO₃) to produce O₃ and secondary organic aerosols; both responsible for the deterioration of the air quality (Meng et al., 1997; Ryerson et al., 2001). In recent studies, both laboratory and intensive measurement campaigns, like that in the tropical forests of Brazil, has been showed that among the VOCs emitted by fires those containing oxygen (OVOCs) dominate with a ratio of 4:1 (Karl et al., 2007). Many OVOCs have very important implications in the chemistry of the atmosphere. Indeed OVOCs such as formaldehyde and acetone, which are the main tropospheric oxidants, have a role in the OH budget. Moreover, in atmosphere, acetone and other OVOC, such as acetaldehyde, can be converted, by oxidative processes, in peroxy radicals (peroxy acetyl nitrate), the precursors of PAN. Observations in various urban sites show that the emissions caused by fires have a role in the degradation of air quality in urban areas such as Zurich and Mexico City, both far from areas subjected to fire (Querol et al., 2008; Weimer et al., 2008). Besides OVOCs emissions, also highly reactive VOCs are

released, such as xylenes, isoprene, monoterpene and sesquiterpenes that are efficient precursors of O₃ and secondary organic aerosols in presence of NO_x (Calfapietra et al., 2009).

Emissions due to natural or deliberate fires of grassland and forest impact the atmospheric composition and aerosol load, both locally and globally. Several field campaigns and continuous observations have confirmed that biomass burning contributes to the degradation of air quality in terms of increase of PM_{2.5}. Carbon emissions during these events are normally split among CO and carbonaceous particles, which in turn may be classified into two main families, e.g. organic carbon (OC) and black carbon (BC) particles. Organics (that normally dominate in mass) are highly soluble, with negligible absorption of the incoming solar radiation (i.e. imaginary part of the refractive index close to zero and single scattering albedo close to unity). On the other hand, BC particles are highly hydrophobic (at least for the first few hours after emission), with strong absorptivity of the incoming radiation (single scattering albedo ~0.2). Fires produce particulate matter (aerosols) also indirectly as product of the oxidation of VOCs emitted. The aerosols formed are of submicrometer in size (Artaxo et al., 2002), they have low deposition rates associated with long lifetime in atmosphere. In some studies, it was shown that organic acids, soluble in water, are important components of the aerosols emitted by fires (Gao et al., 2003; Fuzzi et al., 2007). These organic compounds of the smoke particles are condensation nuclei for cloud droplets with potential impact on the microphysical characteristics of clouds and atmospheric chemistry in the aqueous phase (Andreae and Rosenfeld, 2008). The chemical composition of aerosols emitted by biomass burning has been analyzed in detail in several studies, and during particles aging takes place the condensation of inorganic salts such as sulfates and nitrates, with consequent effects on the budget of reactive nitrogen species (Decesari et al., 2006; Fuzzi et al., 2007).

In recent years, the processes of fire emissions and their influence on the atmospheric composition on local and global scale have been studied in detail, with particular attention to boreal, Amazon and South Africa forest fires (Fuzzi et al., 2007; Kaneyasu et al., 2007; Karl et al., 2007; Verma et al., 2009), as well as summer fires of Southern California (Muhle et al., 2007; Pfister et al., 2008). The nature and mixing ratios of compounds emitted by combustion processes depend on the type of the burned vegetation and on weather conditions during the combustion (Andreae and Merlet, 2001; Langmann et al., 2009). The Mediterranean area, due to high summer temperatures, is the European region in which fires are most frequent. It is also the region where the effects of fire emissions on the atmospheric composition are more evident and of greater interest because of the high intensity of solar radiation. In fact, Southern Europe is the area where the photochemistry of ozone is more active, and where in the past years have been recorded the highest number of exceedances of the thresholds established for ozone (Lelieveld et al., 2002; EEA, 2007). For these reasons, the Mediterranean area is considered a 'hot spot' for the effects of forest fires on the air quality and the factors that modify the climate (Cristofanelli et al. 2009; Cristofanelli et al. 2013).

In this work we report the observations of a campaign conducted in summer 2007 in Southern Europe (L'Aquila, Italy), focusing on the impact of some forest and grassland fires occurred in proximity of the observation site, on the NO, NO₂, O₃, PM_{2.5} and PM₁₀ levels. Fire emissions contribution on the changes of NO₂ and O₃ mixing ratios was studied using a regression model. Improvements on the O₃ simulation including PM_{2.5} data as a proxy of the fire emissions in the model are also discussed.

2. Observation Site

The campaign was carried out in July 2007 at the L'Aquila University buildings, about 3 km northwest from downtown L'Aquila (42°22'N, 13°21'E), a small town of less than 70 000

people in the central part of Italy. The town of L'Aquila is located in a valley at about 700 m above sea level (asl) between the Gran Sasso mountain chain with the highest peak of the Apennines (2 912 m asl), and the Sirente mountain chain (2 348 m asl). The measurement site is far away from strong anthropogenic pollutant sources, such as industries: the main pollution sources are traffic and public and private energy consumption from the town of L'Aquila. Recent analysis shows that the site is mainly impacted by air masses that originate from west to north and is located upwind from the town of L'Aquila, suggesting that the observations are relatively less impacted from local anthropogenic sources (Di Carlo et al., 2007).

3. Air Sampling and Instrumentation

Air was sampled on top of the L'Aquila University building (about 15 m tall) and was drawn down through a 20 m Teflon tube (inner diameter 4.6 mm) at the rate of 6 L/min. All the instruments used in this campaign (NO₂-LIF instrument, O₃ and NO_x analyzers) took the air from the Teflon tube. The residence time in the tube was about 3 s, much shorter than the reaction time between NO and O₃ (about 1 min for 50 ppb of O₃), which assures that no significant chemical conversion occurs before the sampling (Dari-Salisburgo et al., 2009).

NO₂ was measured using a Laser Induced Fluorescence (LIF) system developed at the University of L'Aquila. Briefly, the version of the University of L'Aquila LIF employed in this campaign used a Yag laser to excite NO₂ molecules and, detecting the fluorescence induced in these molecules, the NO₂ mixing ratio is derived directly (Dari-Salisburgo et al., 2009; Di Carlo et al., 2013). In this technique, ambient air is drawn into a detection cell through an orifice to reduce air pressure down to 4–6 Torr, in order to minimize the quenching (non-radiative relaxation of the NO₂ molecules due to collision with other molecules and water vapor) and consequently increase the signal to noise ratio. In the detection cell, the laser beam crosses the ambient airflow and a photomultiplier detects the fluorescence photons (Dari-Salisburgo et al., 2009; Di Carlo et al., 2013). The time resolution of the system was 10 Hz with a detection limit of 3.6 pptv. The first version of the LIF used in this campaign and its evolutions towards a Thermal Dissociation LIF (TD-LIF) used onboard a research aircraft are described in detail in previous papers, reporting instrumental performance and inter-comparison with other systems (Dari-Salisburgo et al., 2009; Di Carlo et al., 2013).

NO and NO₂ were measured using a commercial NO_x chemiluminescent analyzer (Thermo Model 42i TL). NO is measured directly, whereas NO₂ is measured after conversion into NO by means of molybdenum converter heated to 325 °C. Every measurement cycle takes 10 s, 6 s for NO and the remaining for NO₂. The instrument was calibrated before the measurement campaign by a standard procedure using the gas phase titration method.

Ozone was measured with a commercial analyzer Dasibi 1308. It quantifies O₃ mixing ratio by measuring the UV absorption using the Lambert–Beer law. The instrument is equipped with catalytic filter that removes O₃ from the sample air to measure the background before each measurement. The data are updated every 10 s and the precision is 5%.

Mass and number mixing ratios of aerosols were carried out using a multi-channel aerosol laser spectrometer (Grimm analyzer, series 1.108). PM₁₀ is obtained as the total aerosol mass mixing ratios in channels 1 to 13, PM₁ in channels 1 to 7, and PM-coarse as PM₁₀-PM₁ (channels 8 to 13) with an uncertainty of about 20% (Kinne et al., 2003). Data were collected with a 1 min time resolution. Ambient temperature, relative humidity, wind speed and direction, and sun radiation were monitored with a meteorological station close (2 m apart) to the sample point of O₃,

NO and NO₂. Meteorological data were logged every 15 min. In Table 1 all parameters measured during the campaign are reported and, for each of them, minimum, average and maximum values are shown.

Table 1. Parameters measured during the campaign in July 2007 in L'Aquila, including their mean, minimum and maximum value

Parameters	Min.	Average	Max.
O ₃ (ppbv)	6.2	52.8	110.0
NO ₂ (ppbv)	0	5.1	64.1
NO (ppbv)	0	0.4	43.7
PM _{2.5} (µg/m ³)	1.3	15.2	324.9
PM ₁₀ (µg/m ³)	1.4	22.9	406.5
PM coarse (µg/m ³)	0	7.7	371.6
Temperature (°C)	10.0	25.1	37.2
Pressure (hPa)	1 005	1 015	1 024
Relative Humidity (%)	8	38.9	82.0
Wind speed (m/s)	0	8.1	17.0
Wind direction (degree, 0=from North)	0	226.7	350.0
Precipitation (mm)	0	0	0
Global Solar Radiation (W/m ²)	0	417.6	1 510

4. Observations

During the period of the measurements reported here (July 2007), the region around the observation site and most of the Central and Southern Italy were impacted by a relevant number of grassland and forest fires. Summer 2007 was one of the hottest summers for southeastern Europe in recent years, in fact for example, air temperature anomalies of the surface in the period June–August 2007 with respect to the 1961–1990 reference period exceeded between 3 and 4 °C in most of the Southeastern Europe and Balkan Peninsula (Founda and Giannakopoulos, 2009). The environmental emergency has resulted, for the Central and Southern Italy, in 23 dead people, 26 injured, demolished houses, destroyed habitats, landscapes, forests and pastures, everything in ashes. Globally, in summer 2007, in Italy were reported 10 614 fires that have burned an area of 225 563 hectares, of which 115 242 wooded. The average area for each fire was 21.3 hectares, the highest ever recorded from 1970 (RIPALA, 2008). L'Aquila, where the observations reported here were carried out, is the regional Capital of Abruzzo (Central Italy), one of the Italian regions more impacted by fires in the last years. Figure 1 shows the map of the fires occurred during summer 2007 in the Abruzzo region: 274 fires were recorded with 21 167 hectares burned, the highest number of fires and hectares destroyed in the period 2004–2010 (see Table 2) (RIPALA, 2008). Figure 2 shows an image elaborated from reflectance data acquired by MODIS (MODerate resolution Imaging Spectrometer), which is a radiometer installed on-board the TERRA and AQUA satellites. MODIS observes the solar spectrum in the wavelength range between 0.41 and 14.24 µm, using 36 channels with spatial resolution between 250 m and 1 km. Figure 2 shows the plume due to the fires in Abruzzo observed by MODIS on-board the AQUA satellite at 12:05 Local Time (LT) of the 24th July 2007. Among the numerous fire spots active in Abruzzo, the massive one near L'Aquila produced the big plume evident in the MODIS image (Figure 2).

4.1. Data overview

The overview of the main observations carried out during the campaign is showed in Figure 3. The measurements cover the period between the 15th and the 31st of July 2007. In the evening of the 15th July, the first big fire occurred in the surrounding area of L'Aquila, after several other small fires in the same area. The sign of the big fire, which started in the late afternoon, is evident in the NO₂ mixing ratio that, around 19:00 LT, increased from less than

1 ppbv to up to 20 ppbv. The NO₂ increase matches exactly that of PM_{2.5}, with a correlation coefficient (*R*) equal to 0.83 (Figure 4), which confirms that the abrupt change in the NO₂ mixing ratios is due to the fire. The wind direction observed in the site confirms the provenience of the plume from the fire area. On the other hand, the fire plume arrival on the observations site was also visually evident; in fact, a persistent smoke cloud surrounded the site that evening. Before the big fire, of the evening, several spikes in the NO₂ mixing ratio were recorded, due to some other minor fire plumes that reached the measurement site (Figure 4). The elevated mixing ratios of NO₂ and PM_{2.5}, were observed until midnight. The period after the 15th of July (until the 24th of July) was characterized by low mixing ratios of NO₂ and PM_{2.5} with the exception of the 18th of July when the NO₂ mixing ratio increase was not associated to a PM_{2.5} growth, since no fires were reported that day. From the 24th of July there were some other fires around L'Aquila evident from concomitant changes of the NO₂ and PM_{2.5}, especially during the 25th July when, several fires plumes reached the observational site during the day and night. The biggest plume was characterized by a big increase of PM_{2.5}, NO₂ and O₃ in the early afternoon, ozone raised up to 110 ppbv (Figure 3), which is above the European population information threshold of 180 µg/m³ (about 90 ppb). Observations at Mt. Cimone in northern Italian Apennines, during the summer 2007, a month after the measurements reported here, show O₃ peaks higher than 100 ppbv, as observed in L'Aquila (Cristofanelli et al., 2009). The number of plumes that reached the site on 25th of July at different hours of the day is suitable to show the role of NO₂ injection in the O₃ budget. Figure 5 shows the scatter plot between O₃ and NO₂ dividing the observed data between daytime (dominated by photochemistry: production of O₃ from photo-dissociation of NO₂) and nighttime when O₃ is loss due to reaction with NO₂ that produces NO₃. As expected, during daytime O₃ grows following the NO₂ increase, the contrary happens during nighttime (Figure 5).

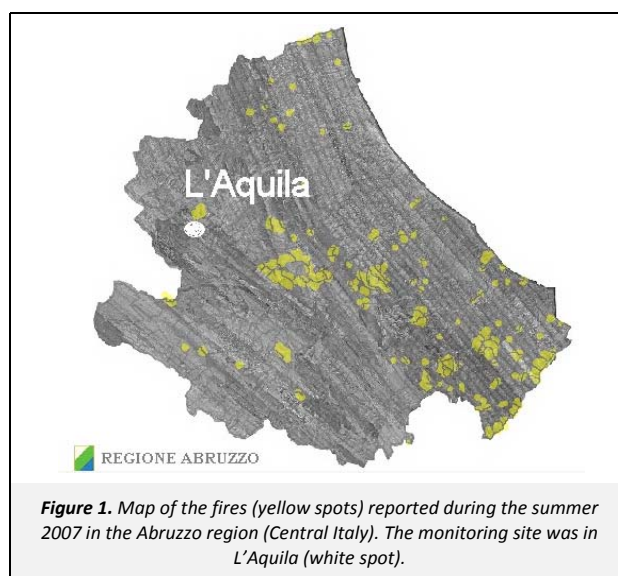
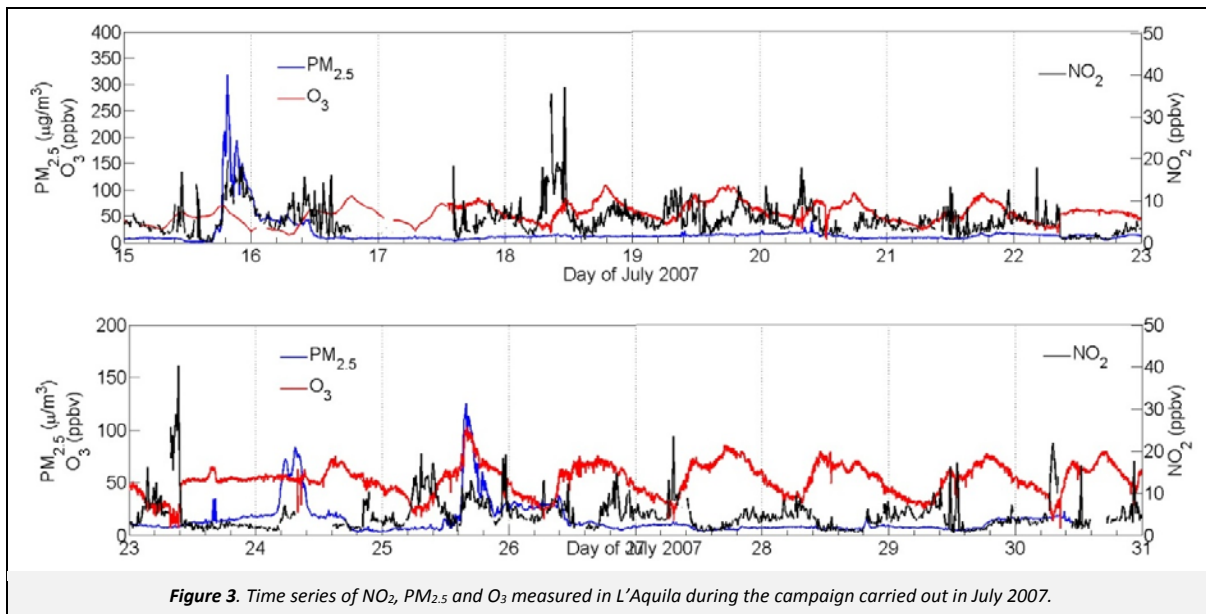
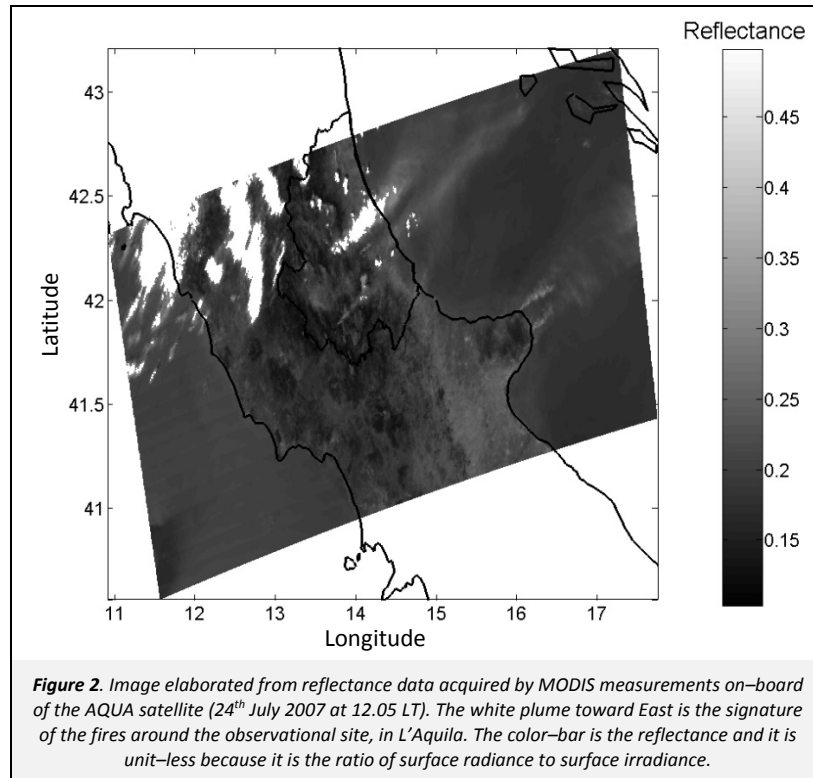


Figure 1. Map of the fires (yellow spots) reported during the summer 2007 in the Abruzzo region (Central Italy). The monitoring site was in L'Aquila (white spot).

Table 2. Number of fires and hectares of forest or grassland destroyed in the Abruzzo region (Central Italy) in the period 2004–2010

Year	Number of Fires	Hectares Burned
2004	54	606
2005	40	347
2006	56	340
2007	274	21 167
2008	159	439
2009	34	159
2010	64	379



4.2. Case study: Application of linear regression models for evaluating the contribution of wildfires emissions on the ozone mixing ratio

To analyze the evolution of the ozone in a period of observations when fire emissions played a big role, we used a linear regression model constrained with observed chemical compounds and meteorological parameters (Sousa et al., 2007). The linear regression model is based on the backward stepwise technique that involves the identification of the best set of parameters to model ozone, and the iterative alteration of the model by adding or removing a predictor variable to maximize the regression coefficients between model and measurements

(Darlington, 1990; Di Carlo et al., 2007; Demuzere et al., 2009; Di Carlo et al., 2009). The strong correlation between NO_2 mixing ratios and $\text{PM}_{2.5}$, observed in a plume emitted from a wildfire (Figure 4) suggests that, besides meteorological parameters, $\text{PM}_{2.5}$ could play a role to simulate the evolution of chemical species impacted by fire emissions. This is something expected, because contrary to other short- or medium-lived fire products (e.g. NO_x , CO, VOC), $\text{PM}_{2.5}$ behaves as an almost perfect passive tracer, considering that the wet deposition of $\text{PM}_{2.5}$ is negligible due to the absence of precipitations during all the observational period, therefore $\text{PM}_{2.5}$ brings the “fire signal” unperturbed over significant distances. The increase of PM due to fire emission is observed in several other sites (Fuzzi et al., 2007; Muhle et al., 2007;

Cristofanelli et al., 2009) including the Mediterranean area (Cristofanelli et al., 2013), while the correlation between PM and NO_2 is reported quite sparsely. To highlight the role of fire emission on the O_3 mixing ratios we compared two days of the observation period: one when a big fire plume reached the observations site (25th of July 2007) and the other (19th of July) with no-fire in the surroundings of the site, nor transported plume from distant areas. For both days we considered measured and modeled O_3 including and excluding $\text{PM}_{2.5}$ mixing ratios as input parameter in the regression model. First, using the stepwise regression technique, we identified the best set of input parameters to be used in the model, excluding redundant, not statistical significant parameters (Di Carlo et al., 2007). Then, at the best set of input parameters, we added $\text{PM}_{2.5}$ mixing ratios as the other input parameter, and run again the regression model to find changes in agreement between observations and model. In this case, for both days, the stepwise technique identifies as “best” set of input data for the regression model: temperature, relative humidity, wind speed, solar radiation, NO and NO_2 . Figure 6a shows the scatter plot between measured and modeled O_3 using the “best” set of input parameters for the day affected by fire plume, whereas Figure 6b shows the same

scatter plot but including $\text{PM}_{2.5}$ mixing ratios as additional input parameter. The inclusion of $\text{PM}_{2.5}$ mixing ratios as an extra input parameter results in a better simulation of the observed O_3 mixing ratios in terms of (1) correlation coefficient that increases of 10% (from 0.88 to 0.97, see Figure 6a and Figure 6b); (2) slope that rises from 0.88 to close to one (0.97), and (3) reduction of the bias of 77% (from 6.48 ppbv to 1.48 ppbv). On the contrary, the inclusion of $\text{PM}_{2.5}$ concentrations as an additional input parameter does not improve the agreement of measured and modeled O_3 for the day not affected by fire plumes (Figure 6c and 6d). In fact, in this case, the slope, bias and correlation coefficient of the regression line of the modeled–measured O_3 do not change with the inclusion of $\text{PM}_{2.5}$ mixing ratios as an extra proxy. These analyses support the hypothesis that in case of fire plume the mixing ratio of O_3 is influenced by fire emissions and on the average this contribution can be quantified in about 5 ppbv (see the 77% bias reduction), about 10% of the daily average O_3 , as in the case study reported here. Moreover, for O_3 observations in a site impacted by a fire plume the quality of modeled O_3 can be improved using fine particles emission as an additional proxy in statistical regression model.

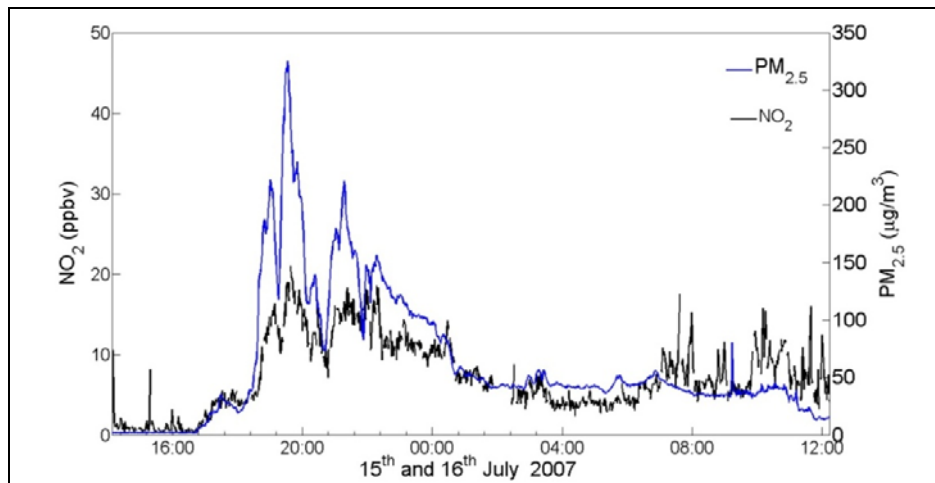


Figure 4. Two days of observations during July 2007 at the University of L'Aquila site. The abrupt increase of NO_2 , well correlated with $\text{PM}_{2.5}$ at about 19:00 LT (196.8 day of the year, 15th of July) is due to transport from intense grassland and forest fires, at about 30 km south–east from L'Aquila.

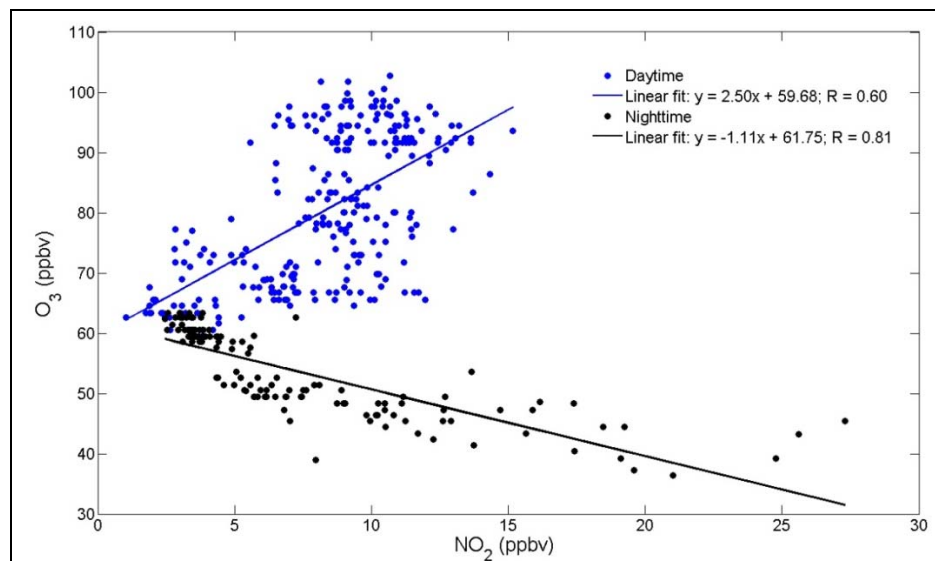


Figure 5. Scatter plot of O_3 and NO_2 dividing daytime from nighttime observed in L'Aquila during the 25th of July 2007, one of the days when different plumes reached the observations site during daytime and nighttime.

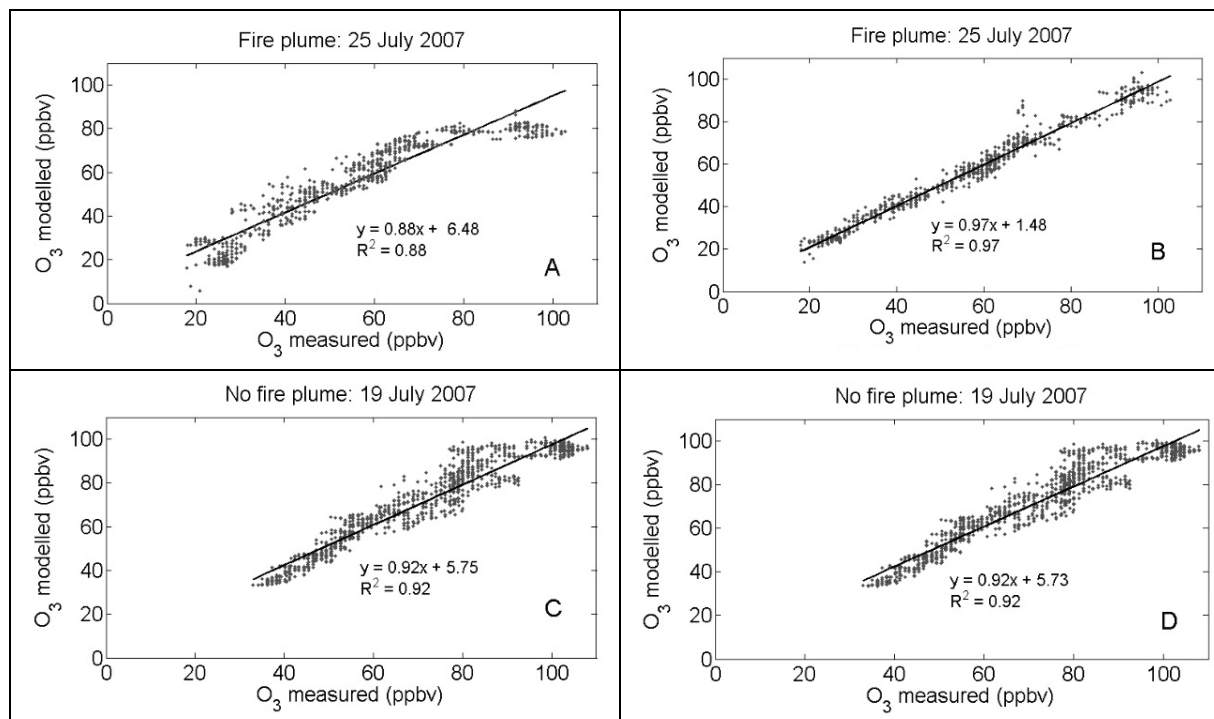


Figure 6. (a) Measured and modeled ozone using as proxy the temperature, relative humidity, and wind speed, solar radiation, NO and NO₂ mixing ratio for a day impacted by fire emissions. (b) Measured and modeled ozone using as proxy the same parameters as in (a) plus PM_{2.5} mixing ratios, for a day impacted by fire emissions. (c) Measured and modeled ozone using as proxy the same parameters as in (a) for a day not impacted by fire emissions. (d) Measured and modeled ozone using as proxy the same parameters as in (a) plus PM_{2.5} mixing ratios, for a day not impacted by fire emissions.

7. Conclusions

In this study, observations of O₃, NO_x and PM result impacted by fire emissions in the vicinity of the observation site. The strong correlation between NO₂ and PM_{2.5} allows to improve the model simulation of O₃, including the mixing ratios of the latter as an additional proxy in a statistical regression model. The improvement is of 77% in terms of bias reduction and 10% in terms of slope and correlation coefficient enhancement between measured and modeled O₃, for a day impacted by fire emissions. The comparison between measured and modeled O₃ in a day impacted by fire emissions and another with no-fire plume, shows that the contribution of fire emission on the O₃ level is, on average, about 10%, at least for the case study reported here. This result suggests the important role of fire emissions in the O₃ budget in background sites with low local anthropogenic emissions, but frequently impacted by forest and grassland fires, like Central Italy and most of the Mediterranean area. However more investigations, especially detecting more fire events to confirm the results reported here, are needed.

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