Atmospheric Pollution Research

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 (NO_2), show a significant increase of NO_2 mixing ratios, in the evening, when a fire plume reached the observations site. The increase of NO_2 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 NO_2 and PM is used to improve the performance of a statistical regression model to simulate the observed O_3, and to highlight the effect of fire emissions on the O_3 mixing ratios. The statistical regression model of O_3 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 NO_2 mixing ratios). A case study, comparing observed and modeled O_3 in different days (with and without fire plume), suggests an impact of fire emissions on the O_3 mixing ratios of about 10%.

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

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1. Introduction

Ozone (O_3) together with aerosols is a tropospheric pollutant and greenhouse gas (IPCC, 2013). In atmosphere, O_3 is produced by the photolysis of nitrogen dioxide (NO_2), which in turn is the result of the oxidation of volatile organic compounds (VOCs) in presence of nitrogen oxide (NO). O_3 production is a non–linear function of the NO_X ($NO+NO_2$) concentrations (Kleinman, 2005), for this reason, the accurate measurement of NO_X is central to study the O_3 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 ($NO_Y=NO+NO_2+RO_2NO_2+RONO_2+HNO_3+2xN_2O_5+HONO+$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 NO_2 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 (CO_2) and carbon monoxide (CO). At the same time, in these combustion processes methane (CH_4), 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 CO_2 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 CO_2. 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 (NO_3) to produce O_3 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 O_3 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, NO_2, O_3, $PM_{2.5}$ and PM_{10} levels. Fire emissions contribution on the changes of NO_2 and O_3 mixing ratios was studied using a regression model. Improvements on the O_3 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 us 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 (NO_2–LIF instrument, O_3 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 O_3 (about 1 min for 50 ppb of O_3), which assures that no significant chemical conversion occurs before the sampling (Dari–Salisburgo et al., 2009).

NO_2 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 NO_2 molecules and, detecting the fluorescence induced in these molecules, the NO_2 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 NO_2 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 NO_2 were measured using a commercial NO_X chemiluminescent analyzer (Thermo Model 42i TL). NO is measured directly, whereas NO_2 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 NO_2. 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 O_3 mixing ratio by measuring the UV absorption using the Lambert–Beer law. The instrument is equipped with catalytic filter that removes O_3 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). PM_{10} is obtained as the total aerosol mass mixing ratios in channels 1 to 13, PM_1 in channels 1 to 7, and PM–coarse as PM_{10}–PM_1 (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 O_3,