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Influence of the aerosol solar extinction on photochemistry during the 2010 Russian wildfires episode

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Abstract

In this work, impact of aerosol solar extinction on the photochemistry over eastern Europe during the 2010 wildfires episode is discussed for the period from 5 to 12 August 2010, which coincides to the peak of fire activity. The methodology is based on an on-line coupling between the chemistry-transport model CHIMERE (extended by an aerosol optical module) and the radiative transfer code TUV. Results of simulations indicate an important influence of the aerosol solar extinction, in terms of intensity and spatial extent, with a reduction of the photolysis rates of NO_2 and O_3 up to 50 % (in daytime average) along the aerosol plume transport. At a regional scale, these changes in photolysis rates lead to a 3–15 % increase in the NO_2 daytime concentration and to an ozone reduction near the surface of 1–12 %. The ozone reduction is shown to occur over the entire boundary layer, where aerosols are located. Also, the total aerosol mass concentration (PM10) is shown to be decreased by 1–2 %, on average during the studied period, caused by a reduced formation of secondary aerosols such as sulphates and secondary organics (4–10 %) when aerosol impact on photolysis rates is included. In terms of model performance, comparisons of simulations with air quality measurements at Moscow indicate that an explicit representation of aerosols interaction with photolysis rates tend to improve the estimation of the near-surface concentration of ozone and nitrogen dioxide as well as the formation of inorganic aerosol species such as ammonium, nitrates and sulphates.

1 Introduction

For several years, it has been well recognized that air pollution of gaseous and particulate origin can have adverse health effects (Miller et al., 2012; Beelen et al., 2014). In consequence, efficient air pollution control strategies have now become a challenge for environmental policies. In the context of air quality monitoring, the exceedance of

certain thresholds of pollutant concentrations is a criterion often used by authorities of a country to prevent people from air pollution exposure. In general, the exceedance of these thresholds is evaluated from air quality numerical forecast such as in France where the regional chemistry-transport model CHIMERE (Menut et al., 2013) is used in the French national air quality forecasting and monitoring system known as PREV'AIR (Honoré et al., 2008). Photochemical pollutants (ozone, secondary aerosols,...), which are formed from photo-dissociation of precursors such as nitrogen dioxide (NO_2) and volatile organic compounds (VOC) (Jenkin and Clemitshaw, 2000), are of particular interest for air quality monitoring (Honoré et al., 2008) due to their negative impacts on both environment and human health (Amin, 2014; Hunova et al., 2014).

The key parameter that governs the photo-dissociation of photochemical precursors in the atmosphere is the photolysis rate, which mainly depends on the available actinic flux (Seinfeld and Pandis, 2006). Aerosols are known to have large influence on the available actinic flux by interacting with solar radiation in the ultraviolet-visible wavelengths (Li et al., 2011a,b; Lou et al., 2014). For example, Wai and Tanner (2010) showed, by using a combination of remote sensing observations and chemical-transport model, that aerosol solar extinction could lead to a 7–32 % reduction in maximum ozone concentration over Hong-Kong during highly polluted days. Also, Li et al. (2011b) highlighted, with WRF-CHEM modelling experiments, that changes in photolysis rates due to the presence of particles led to a decrease of about, respectively, 2–17 % and 5–6 % in daytime ozone and secondary aerosols (nitrate, secondary organics) concentrations over Mexico City during the 2006 Megacity Initiative: Local and Global Research Observations (MILAGRO) campaign.

To reduce computational time for operational purpose, one major characteristic of air quality modelling platforms is that impacts of aerosols and clouds on solar radiation are often taken into account as simplified attenuation factors when evaluating the photolysis rates (Honoré et al., 2008; Menut et al., 2013). However, Real and Sartelet (2011) highlighted that simplified parametrization of aerosol impact on photolysis rates could tend to worsen air quality model performance in simulating ozone and particulate con-

centration, especially under highly polluted environments.

The aim of the present study is to implement, in the chemistry-transport model CHIMERE, an explicit representation of the alteration of photolysis rates by aerosols and discuss the impact in terms of modelled ozone budget and the formation of secondary aerosols at regional scale. We focus on a major fire event that occurred in Russia during August 2010 as its episode was characterized by important concentrations of primary and secondary aerosols and large concentrations of ozone, especially over this specific region (Zvyagintsev et al., 2010; Konovalov et al., 2011; Popovicheva et al., 2014). Also, the study of Chubarova et al. 2012 clearly shows that, during this specific wildfire episode, the aerosol optical thickness over the Moscow region was more than three times larger than the one observed during typical August conditions over the period 2001–2010. This suggests that, even if anthropogenic aerosols are present over the studied region, the contribution of smoke aerosols during this specific event is very large. Then, this case study represents an excellent opportunity to discuss how aerosol solar extinction, especially biomass burning particles, can affect photochemistry. Fires can affect atmospheric chemistry in several ways. They emit primary gaseous pollutants (such as CO, OH, NO, NO_2 and volatile organic compounds) that can react in the atmosphere to form ozone and other pollutants (Turquety, 2013). They also released aerosols that can directly affect air quality or indirectly by acting as a medium in complex heterogeneous reactions (Slade and Knopf, 2013; Nie et al., 2015). Finally, they can affect the intensity of solar radiation, which in turn could affect photochemistry of the atmosphere. The latter impact is the subject of the present study.

The approach is based on an on-line coupling between the regional model CHIMERE, extended by an aerosol optical module (Péré et al., 2010), and the Tropospheric Ultraviolet and Visible (TUV) radiation model (Madronich and Flocke, 1998). In this methodology, the aerosol optical thickness, single scattering albedo and asymmetry parameter are first modelled by CHIMERE using an aerosol core-shell mixing hypothesis, as in Péré et al. (2009, 2010). This mixing approach has been previously used by Péré et al. (2014) to study the 2010 Russian wildfires direct radiative forcing and its feedback on

the regional atmospheric dynamics. Results indicate that it can give a good representation of the absorption properties of particles during this specific period. In a second time, aerosol optical properties are used as inputs in the radiative transfer code TUV to evaluate the impact of aerosol short-wave solar extinction on photolysis rates and the formation of ozone and secondary particles. The advantage of such methodology is the use of two specific state-of-the-art models to explicitly simulate the interaction of physical-chemically resolved aerosols with the actinic flux and the associated impact on modelled photolysis rates and photochemistry.

Section 2 describes the configuration of each model as well as the development of their on-line coupling. In Section 3 are discussed modelled regional changes in the near surface concentrations of NO_2, O_3 and secondary aerosols over Russia induced by modifications of photolysis rates by smoke aerosols during August 2010. Finally, conclusions and perspectives of future works are given in Section 4.

2 Methodology

2.1 Description of the CHIMERE model

2.1.1 Aerosol module

CHIMERE is a state-of-the-art 3D chemistry transport model that calculates the concentrations of numerous gaseous and particulate pollutants (Vautard et al., 2001; Menut et al., 2013). The dynamics and gas phase parts of the model is regularly improved (Menut et al., 2013) and its documentation can be downloaded at http://www.lmd.polytechnique.fr/chimere/. In this work, the CHIMERE domain has a 30 km horizontal resolution and ranges from 43.40^{o}N to 63.20^{o}N in latitude and from 18.70^{o}E to 57.30^{o}E in longitude. The aerosol part is described by Bessagnet et al. (2004) and is composed of 10 chemical species: sulphates, nitrates, ammonium, primary organic and black carbon (OC and BC), secondary organic aerosols (SOA), sea salt, natural and anthropogenic

dust and water. The evolution of aerosols is described with a 8-bins size distribution (from about 40 nm to 10 μm in diameter) and includes the main physical processes such as nucleation, coagulation, condensation/evaporation, adsorption/desorption, wet and dry deposition and scavenging.

Anthropogenic emissions of gaseous and particulate origin come from the EMEP database. Concerning OC and BC emissions, the inventory of Junker and Liousse (2008) has been used. Natural soil dust are dynamically produced within the domain according to the methodology of Vautard et al. (2005). SOA formation is represented through oxidation processes of relevant precursors of biogenic and anthropogenic origin and gas particle partitioning schemes (Bessagnet et al., 2008). VOC and NO emissions from vegetation are calculated using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006). Aerosols and gases emitted by wildfires affecting Russia during 2010 are taken into account following the work described and validated by Kaiser et al. (2012). It consists in the assimilation of the fire radiative observations from the Moderate Resolution Imaging Spectroradiometer into the Global Fire assimilation System combined with the use of specific combustion rate and emission factors to estimate biomass burning emissions. More information on the methodology as well as a validation study for the 2010 Russian wildfires episode can be found in Kaiser et al. (2012).

CHIMERE is forced at these boundaries by monthly climatologies, calculated over the 2000–2004 period, of the main gases and particles provided by the MOZART (Horowitz et al., 2003) and LMDzT–INCA global chemistry-transport models (Hauglustaine et al., 2004), respectively. The evaluation study of Péré et al. (2014) showed that the fire inventory of Kaiser et al. (2012) used in this work combined with the CHIMERE model have been shown to well capture the evolution of the Russian fire plume during the studied period, suggesting a low influence of these boundary conditions. Also, CHIMERE is off-line driven by the Weather Research and Forecasting model (WRF) at a 30 km resolution. The version 3.1 is used in this study with the same configuration as in Péré et al. (2011). It has 27 vertical levels from 40 m to about 20 km and

includes the following parametrizations: the WRF single-moment five-class scheme of Hong et al. (2006) for the microphysics module, the Kain–Fritsch cumulus parametrization (Kain, 2004), the NOAH land surface module of Chen and Dudhia (2001) and the Yonsei University planetary boundary layer scheme (Hong et al., 2006; Hong, 2007).

2.1.2 Modelling aerosol optical properties

The calculation of optical properties of particles is the pre-requisite for the evaluation of their impacts on photolysis rates and photochemistry as they provide information on how aerosols will interact with the actinic flux. In that sense, we developed a numerical scheme dedicated to calculate aerosol optical properties from aerosol concentrations, size distribution and chemical composition modelled by CHIMERE. A complete description of this optical module is presented in the work of Péré et al. (2010). To compute the complex refractive index of a particle, the hypothesis of a core-shell mixing has been chosen with a core of primary species (BC, OC and dust) surrounded by a shell of secondary ones (sulphates, nitrates, ammonium, secondary organics) and sea salt and water. This mixing choice is supported by recent studies giving evidence of coatings of secondary particles on black carbon aerosols over Europe (Vester et al., 2007; McMeeking et al., 2011). Also, such mixing has been shown to correctly reproduce the absorbing properties of aerosols during the 2010 Russian wildfire episode (Péré et al., 2014). For each size bin, a volume average procedure is used to calculate the refractive index of the core and the shell (Lesins et al., 2002) which is then used as inputs in the Mie algorithm for n-layered spheres of Wu and Wang (1991) to calculate the scattering and absorption coefficients. It should be noted that the volume of the core and the shell can vary during the simulation in function of the different physical processes influencing aerosol population. The optical properties of the total aerosol distribution needed in radiative transfer modelling, such as the Aerosol Optical Thickness (AOT), Single Scattering Albedo (SSA) and asymmetry parameter (g), are calculated as in Wu et al. (1996).

A detailed evaluation of the optical module for the 2010 Russian wildfire episode by

using different sets of measurements is presented by Péré et al. (2014). Only a sum-up is given here. Figure 1a-b presents the temporal evolution of the AOT between 5 and 12 August 2010 modeled by CHIMERE at 500 nm and measured by the Terra MODIS (Moderate Resolution Imaging Spectroradiometer) satellite sensor at 550 nm. The simulated 850 hPa wind is also indicated. As shown by the 850 hPa wind fields, meteorological conditions were characterized by an important anticyclonic system over central Russia which favored the re-circulation and accumulation of pollution from intensive wildfires and anthropogenic origin (Witte et al., 2011). MODIS observations highlight this intense particulate pollution episode with AOT (550 nm) above 1 over large areas and values up to 4 along the transport of the aerosol plume. This plume was advected in the anticyclonic flow from the source region (east of Moscow) towards Moscow and the northern part of the area (6–10 August) and back to the east on 10–12 August. Although the maximum AOT value observed by MODIS is underestimated by CHIMERE, we can see that the model is able to reproduce the main aerosol plume features in terms of transport and intensity during this specific period, with a spatial correlation of 0.4–0.8 and a normalized mean bias of -(15–40) % depending of the day. Some minor discrepancies between CHIMERE and MODIS can be seen, such as local AOT underestimations within the intense plume or some overestimations near the source region. These AOT biases may induce local under or overestimation of the aerosol solar extinction simulated by CHIMERE and its potential impact on the photolysis rates discussed on Figures 3 and 4. The altitude of transport was shown to be below 5 km and comparisons between CHIMERE and CALIOP show good consistency, as discussed in further details hereafter on Figure 8. Figure 2 indicates that the transport of this intense aerosol plume over Moscow between 6 and 10 August 2010 has been recorded in the AOT measurements of the Moscow AERONET station. We can see that a large enhancement of the particulate pollution is detected over Moscow when the plume overpasses the area, with an AERONET AOT (440 nm) from 0.56 on 5 August to 2–4 between 6 and 10 August. Then AOT decreases to moderate values (0.4–0.7 at 440 nm) on 11–12 August when the intense aerosol plume leaves the re-

gion. CHIMERE simulates rather well the temporal evolution of the AOT over Moscow during this period with biases from -53 % to 8 %, except for the 6 and 10 August. For these two days, the model underestimation is of 60–75 % due to some model deficiencies in simulating the transport of the intense aerosol plume over Moscow. During the study period, Péré et al. (2014) showed that organics species are the dominant part of the aerosol composition simulated by CHIMERE over Moscow with relative contributions of 8–67 % and 16.5–75 % for, respectively, primary organic carbon and secondary organic aerosols. OC is the major chemical species between 5 and 10 August (43–67 %) while SOA dominates at the end of the period (71–75 %) when the aerosol plume moves away from Moscow. These elevated proportions of organic carbon are the result of large OC and VOC (Volatil Organic Compounds) emissions (mainly from wildfires with also an anthropogenic contribution) combined with an important photochemistry favored by persistent sunny conditions. BC particles are present in a much lower fraction (0.4–0.8 %). This important contribution of scattering organic aerosols lead to high SSA modeled over Moscow throughout the period, with values of 0.97 (between 300 nm and 1000 nm), in good agreement with AERONET measurements over Moscow (0.95–0.96 between 440 nm and 1020 nm). Such elevated SSA associated to large proportion of organic species is supported by recent studies. High SSA values (0.95 in the visible spectrum) have been measured during this specific fire episode by Chubarova et al. (2012) and are typical of peat fires and smoldering conditions. Also, Popovicheva et al. (2014) highlights, with physical-chemical measurements, that the aerosol composition over Moscow during the 2010 fire episode is dominated by organic species with a low fraction of black carbon. Globally, the comparisons between aerosol simulation and measurements data highlighted the ability of the model to give an appropriate representation of the aerosol size distribution and scattering/absorption properties (Péré et al., 2014), which is the pre-requisite to evaluate its influence on photolysis rates and the formation of photochemical pollutants.

2.2 Description of the TUV model

TUV is a widely-used state-of-the-art radiative transfer model developed at the National Centre for Atmospheric Research (Madronich and Flocke, 1998). In this study, we used the version 4.6 of the code (released in March 2009) freely available at the website: http ://cprm.acd.ucar.edu/Models/TUV/. The model calculates the actinic flux and photolysis rates of a large number of photochemical species.

Photolysis is the process breaking the covalent bond of some reactive gaseous species by short-wave solar radiation. This process is very important in the atmosphere as it controls the abundance of numerous air pollutants such as ozone and nitrogen dioxide. The photolysis rate of a given specie J (s^{-1}) is calculated as follows:

$$J(s^{-1}) = \int_{\lambda_1}^{\lambda_2} \sigma(\lambda,T).\phi(\lambda,T).F(\lambda)d\lambda \quad (1)$$

where $\sigma(\lambda$,T) and $\phi(\lambda$,T) are, respectively, the absorption cross section (cm^2) and the quantum yield of a given molecule, T the air temperature (K) and F(λ) the actinic flux between wavelengths λ_1 and λ_2 (photons.cm^{-2}.s^{-1}.nm^{-1}). The absorption cross section reflects the probability of collision between a photon and the molecule, while the quantum yield is the probability that the molecule is dissociated after collision with a photon. The dependence of both parameters on the air temperature is calculated by TUV by using the vertical profile of air temperature issued from the meteorological model WRF used to drive CHIMERE.

The actinic flux is calculated by integrating the solar flux over all sphere angles considering 5646 wavelengths between 120 nm and 1250 nm. When going through the atmosphere, the actinic flux can be attenuated by molecular absorption and diffusion but also by the presence of clouds and aerosols. For clouds and aerosols, the attenuation is calculated by using their respective aerosol optical thickness, single scattering

albedo and asymmetry parameter. In TUV, clouds are assumed to be horizontally homogeneous layers and are considered to be of three types : low, middle and high altitude clouds. Altitudes of their bases and tops as well as their optical thicknesses are estimated by the meteorological model WRF. The single scattering albedo and asymmetry parameter are considered constant in the UV–visible wavelengths and are taken equal to, respectively, 0.99 and 0.85 for the three types of clouds (Madronich and Flocke, 1998). It should be noted that changes in the cloud optical properties due to the activation of aerosols into cloud condensation nuclei are not taken into account in our approach. However, the anticyclonic conditions that prevailed over eastern Europe during the studied period suggest a low impact of clouds on the modelled actinic flux and photolysis rates (Lau and Kim, 2012).

Concerning aerosols, the three optical properties (AOT, SSA and g) are calculated at 200, 300, 400, 500, 600 and 700 nm using the aerosol optical module and then interpolated to the TUV wavelength grid (120–1250 nm). To solve the radiative transfer equation and compute the actinic flux along the atmospheric column, the Eddington approximation has been chosen in TUV as it allows an accurate estimation of modelled radiative fluxes (Joseph et al., 1976).

Recently, Palancar et al. (2013) realized a intercomparison exercise between the TUV model and UV actinic flux measurements over Mexico during the MILAGRO campaign. They highlighted the good performance of the model in reproducing observations both at the surface and in the lower troposphere over this highly polluted area. This validation study gives confidence in our estimation of photolysis rates perturbations by aerosols during the 2010 Russian wildfires presented hereinafter.

2.3 Simulation set-up

The methodology developed in this study consists of a one-way and on-line coupling between TUV and CHIMERE. In this approach, the radiative transfer code TUV has been implemented within CHIMERE so that each model runs simultaneously. During

the simulation, the aerosol optical properties modelled by CHIMERE for a core-shell mixing (AOT, SSA, g) are used as inputs in TUV in order to take into account the influence of aerosol solar extinction on photolysis rates. Then, the photolysis rates estimated by TUV are in turn used by CHIMERE to calculate the concentrations of photochemical pollutants.

Two simulations are performed for the period of peak fire activity (5–12 August 2010):
(1) In the first one, the attenuation of actinic flux is only due to gases and clouds: CHIMERE–TUV(gases+clouds).
(2) In the second one, the impact of aerosols on solar extinction is added in the photolysis rates calculation: CHIMERE–TUV(gases+clouds+aerosols).
The impact of aerosols on photolysis rates and associated concentrations of photochemical pollutants are then estimated by differencing the two simulations: (2) - (1). It should be noted that adding the aerosol impact on solar extinction in simulation (2) induces a computation time increase of 50 % compared to the simulation (1).

We will focus on the aerosol impact on NO_2 and O_3 photolysis rates, which mainly drives the concentration of ozone, NO_2 and OH radicals in the troposphere. Indeed, the major source of ozone is the result of the NO_2 photolysis:

$$NO_2 + \hbar.\vartheta \longrightarrow NO + O(^3P) \qquad J[NO_2] \tag{2}$$

followed by the reaction of O(^{3}P) with a dioxygene molecule (M is a third body favouring the reaction):

$$O(^3P) + O_2 + M \longrightarrow O_3 + M \tag{3}$$

Given that reaction (3) is rapid, the formation rate of ozone is mainly determined by the constant rate J[NO_2]. In parallel, the major sink of ozone during daytime is its photodissociation following the reaction:

$$O_3 + \hbar.\vartheta \longrightarrow O_2 + O(^1D) \qquad J[O_3] \tag{4}$$

$O(^1D)$ will rapidly react with a water molecule to form OH radicals:

$$O(^1D) + H_2O \longrightarrow 2OH \quad (5)$$

The latter reaction is a major source of OH radicals in the troposphere. They are involved in the formation of secondary particles as oxidants of their gaseous precursors. For example, they contribute to the oxidation of SO_2, NO_2 and VOC, which can result in the formation of, respectively, sulphate, nitrate and secondary organic aerosols. The sequence of reactions (R1 to R4) is generally initiated by the reaction of various VOC with the OH radical.

3 Results and discussion

3.1 Regional impact of the 2010 Russian wildfires on the formation of ozone and nitrogen dioxyde

During the wildfire episode, the important concentrations of scattering aerosols have affected significantly the UV-visible solar radiation in terms of intensity and spatial extent. Figures 3a-b and 4a-b report the daytime average percentage changes in near surface photolysis rates of NO_2 and O_3, respectively. Changes are shown to be negative over the entire area with mean daytime values between -2 % and -50 % and closely follow the AOT spatial features (see Figures 1a-b). It is interesting to note that the impact of the aerosol solar extinction is more pronounced for J[O_3] than for J[NO_2], for each day of the studied period. For both photolysis rate, the largest reduction is simulated along the transport of the aerosol plume (20–50 %). The photochemistry over the Moscow region has also been affected, especially during the arrival of the aerosol plume between 6 and 10 August 2010. This point will be discussed in further details hereafter. These modelled changes obtained here are comparable with the recent study of Real and Sartelet (2011) in which they simulate, by using the chemistry-transport model

Polyphemus-Polair3D coupled with the radiative transfer code Fast-J, a reduction of J[NO_2] and J[O_3] reaching 30 % (in monthly mean) during summer 2001 over European regions characterized by elevated AOT (0.6–0.7 at 550 nm). Also, Hodzic et al. (2007) simulated a 15–30 % NO_2 photolysis reduction during the 2003 European summer heatwave in case of absorbing biomass burning aerosols (AOT(550 nm) = 0.7–0.8, SSA (532 nm) = 0.83–0.87).

According to equations 2 to 4, the alteration of J[NO_2] and J[O_3] in the presence of aerosols suggests, in turn, a modification of their concentrations near the surface. Figure 5 gives an example of these corresponding changes during the 8 August for NO_2 and O_3. Some notable modification of the NO_2 concentration is simulated, as it is mainly driven during daytime by its photolytic destruction (see equation 2). The important diminution of J[NO_2] due to aerosols (between 2 and 50 %) leads to an increase of its near surface concentration reaching, in average, 3 to 15 %. Concerning ozone, its daytime concentration is influenced by both variations of J[NO_2] (source of ozone, see equations 2 and 3) and variations of J[O_3] (sink of ozone, see equation 4). We can deduce from figure 5 that the influence of J[NO_2] reduction seems to slightly dominate the influence of J[O_3] reduction, resulting in a decrease of the near surface concentration of ozone between 1 % and 12 %. These results are comparable to those obtained by Real and Sartelet (2011) who simulated a 4–8 % reduction of near-surface ozone concentration (for July 2001) over areas where the decrease of J[NO_2], due to the aerosol solar extinction, reached 30 %. Also, Mena-Carrasco et al. (2009) highlighted, by combining STEM-2K3 model experiments and aircraft observations from the MILAGRO campaign during March 2006, a 40 % attenuation of J[NO_2] associated to an intense aerosol plume over Mexico City, resulting in a 5–10 % diminution of ozone production. Such impacts are however less pronounced than the ones obtained over some highly polluted Asian regions. For example, Bian et al. (2007) and Wai and Tanner (2010) showed, over China, a reduction of maximum ozone concentration reaching 30 % to 70 % associated to similar aerosol loadings as obtained in our study ($1 <$ AOT(550 nm) < 2.5). The low absorbing properties of the Russian smoke plume (Péré et al., 2014)

could be a reason for such a behaviour.

To further investigate aerosol feedback on the ozone cycle and the formation of secondary particles, we will now focus our study on the Moscow region where the aerosol solar extinction is pronounced, especially during the aerosol plume overpass (6–10 August 2010). Gaseous and particulate measurements from the Moscow air quality station will also be used in the analysis.

3.2 Impact of the 2010 Russian wildfires on the photochemistry over Moscow

On Figure 6, the impact of particles on the formation of ozone and nitrogen dioxide over Moscow is discussed in terms of daytime average percentage changes in their near-surface photolysis frequencies and concentrations as a function of modelled AOT (440 nm). As expected, changes appear to have a good linearity with AOT (440 nm) with a correlation of 0.90–0.95, i.e modifications become more important when the aerosol loading increases. As shown previously over the entire area, J[O_3] is more sensitive to the presence of particles (reduction of about 10 % per unit of AOT) than J[NO_2] (reduction of about 6 % per unit of AOT). These modifications of photolysis rates result in an increase of the ground NO_2 concentration of 3 % (per unit of AOT). Response of the ozone concentration under the aerosol radiative influence is more complex. Indeed, ozone formation is driven by two major precursors: nitrogen oxides (NOx = NO + NO_2) and volatile organic compounds (VOC) in a complex photochemistry. However, it is possible to identify two regimes of ozone formation by looking at the ratio between the concentrations of VOC and NOx : A NOx-limited and a NOX-saturated regime (Seinfeld and Pandis, 1998). Based on the study of Dodge (1977) on ozone chemical mechanisms, a VOC(ppmC)/NOx(ppm) ratio below 4 defines a NOx-saturated environment. Figure 7 indicates that such photochemical regime occurred over Moscow during the studied period, with a VOC(ppmC)/NOx(ppm) ratio always below this threshold. In this case, inclusion of the aerosol radiative impact on photochemistry leads to two antagonists responses : (1) Increase of NOx concentration trough reduction of photolysis

rates is unfavourable to ozone formation in a NOx-saturated environment. In parallel, (2) reduction of the ozone photolysis is favourable to its accumulation. The overall impact of aerosols on the ozone concentration is then small due to these two antagonist responses, about 1 % per unit of AOT (see Figure 6).

The influence of aerosols on photochemistry does not only occur at the surface but also in the low troposphere, as illustrated in Figure 8. This figure presents the aerosol extinction coefficient (in km^{-1}) modeled by CHIMERE and retrieved by CALIOP for the 9 August inside and outside the intense aerosol plume (see Figure 1 for the localisations of these 2 points). The vertical profile of the daytime average percentage changes in the ozone concentration due to this intense aerosol plume is also indicated. We can see that inside the intense fire plume, more than 70 % of the aerosol extinction is measured below the first two kilometres of the atmosphere with values reaching 0.5–0.95 km^{-1}, indicating a low altitude transport. Above, CALIOP aerosol extinction gradually decreases to become negligible at an altitude of 5 km. For comparison, outside the intense fire plume, particles remain confined near the ground, with a much lower aerosol extinction (maximum value of 0.15 km^{-1} at an altitude of 200 m), suggesting a prevailing anthropogenic origin. CHIMERE compares well with CALIOP extinction coefficients within the uncertainty range of measurements for both cases, giving confidence in the estimated impact of aerosols on the ozone reduction. This ozone reduction, due to the presence of the intense aerosol plume, is maximum (4–5 %) below an altitude of 2 km where most of the aerosol extinction occurs and then gradually decreases with the altitude.

In terms of model performance, it is interesting to see if an explicit representation of aerosol impact on photolysis rates tend to improve the simulation of the concentration of photochemical pollutants, compared to a simulation without aerosol feedback. For such analyse, statistical comparisons between the near-surface concentrations of NO_2 and O_3 simulated with and without aerosols and measured at Moscow by an air quality station has been made. Results are presented in Tables 1 and 2 for hourly values and daily maximum values, respectively. We can see that, for both configura-

tions, scores for ozone and NO_2 are of 48-88 $\mu g/m^3$ for the RMSE and of 0.22–0.60 for the temporal correlation. Such biases could be the consequence of possible uncertainties in the EMEP anthropogenic emission inventory used in the present study. Indeed, it should be noted that Bessagnet et al. (2014), who performed an extensive intercomparison study between several European state-of-the-art chemistry-transport models (including CHIMERE) and EMEP measurements, also showed a model NO_2 and ozone underestimation over Europe in the frame of the EURODELTA III project. The model biases on these two species can induce a bias on the modelled photolysis rates as gaseous pollutants (especially NO_2) may also influence actinic flux through direct absorption. Unfortunately, quantifying this bias would require to compare simulated values of actinic flux with observations, which is not possible for this study as no such measurements are available to us for this specific event. However, a recent study by Palancar et al. (2013) estimated the relative influence of aerosols and NO_2 on the actinic fluxes by comparing measurements made during the MILAGRO campaign over Mexico City with TUV model calculations. Comparisons indicate that aerosols and NO_2 account for, respectively, 70 % and 25 % of actinic fluxes reduction observed at the surface. Hence, such results suggest a moderate impact of the O_3 and NO_2 CHIMERE biases on the photolysis rates simulated over Moscow during the 2010 wildfires episode. Overall, Tables 1 and 2 indicates that the inclusion of aerosols in the simulation improves the correlation and slightly reduces biases with measurements for both species and for both hourly and maximum values.

To further investigate the aerosol feedback on the ozone daytime cycle, Figure 9 displays the temporal evolution (between 5 and 12 August 2010) of the near-surface ozone concentration (in $\mu g/m^3$) modelled with and without aerosol feedback along with corresponding observations at the Moscow monitoring station. This figure confirms the moderate overall impact of the aerosol solar extinction on the ozone production, with a maximum diminution reaching 7–10 % during the aerosol plume overpass (7, 8 and 9 August), which leads to slightly reduce the bias between model and observations. Depending on the day, the model simulates lower or higher hourly values compared to

observations. The ozone model biases presented on Figure 9 clearly show that some processes are missing and/or not well represented in the CHIMERE model. Among these processes, adding the aerosol direct radiative impact on the simulation of photolysis rates could improve the estimation of ozone formation for some days. However, it is obvious that this process does not entirely explain model biases. As indicated previously, uncertainties on the EMEP emission database for this specific region could be a possible reason for these biases. Also, the model is shown to overestimate nighttime concentrations over the period, which could be due to uncertainties in correctly estimating its dry deposition and titration by NO, as previously highlighted by Honoré et al. (2008) over Western Europe. It should be noted that a inadequate representation of the nocturnal air ventilation could also be a reason for such a model bias.

In parallel, the presence of aerosols tends to reduce the oxidising capacity of the atmosphere (through reduction of OH radicals, see equation 5), which leads to decrease the formation of secondary aerosols. As illustrated in figure 10a, the maximum reduction in the near-surface concentrations of sulphates (oxidation product of SO_2) and SOA (oxidation product of VOC) occurs on 8 August with daytime average values of 10 % and 4 %, respectively. For this day, figure 10b shows that these changes are mainly due to a reduced formation of very fine particles, i.e with a diameter comprised between 40 nm (bin 1) and 300 nm (bin 4). The overall impact is then a slightly reduction of the total aerosol mass concentration (PM10) comprised between 1 and 2 % over the entire period (Figure 10a). These results are comparable to the findings of Real and Sartelet (2011) and Li et al. (2011b) who showed a 5–10 % reduction of the formation of secondary aerosols due to the aerosol solar extinction, in case of intense particulate pollution over, respectively, Europe and Mexico City. As for NO_2 and O_3, including the optical effect of aerosols in the photolysis calculations slightly improves the formation of secondary inorganic species in the CHIMERE model with a RMSE systematically reduced (see Table 3). The large overestimation of sulphate concentrations is slightly decreased and the simulated concentrations of ammonium and nitrates get closer to the observed one. However, the correlations are not always improved when

taking into account the aerosol radiative influence. The large overestimation of scattering sulphates particles is expected to have a low influence on the estimation of aerosol impact on photolysis rates as this chemical specie represents less than 10 % of the total chemical composition modelled over Moscow during the study period (Péré et al., 2014). This is confirmed by the excellent agreement between modelled and measured SSA during this specific event (as discussed in section 2.1.2), which is a key factor in the determination of particle's interaction with the actinic flux. Even if some discrepancies between measurements and model simulation results can be present, Table 3 suggests that taking into account the aerosol solar extinction in the photolysis calculation can improve the model capacity to reproduce the photochemistry under polluted environments.

4 Conclusions

In the present study, we have developed an on-line coupling between the chemistry-transport model CHIMERE (complemented by an aerosol optical module) and the radiative transfer code TUV to study the impact of aerosol solar extinction on the photochemistry over eastern Europe during the 2010 wildfires episode. Simulations from 5 to 12 August 2010, corresponding to the peak of fire activity, have been performed with and without aerosol impact on photolysis rates and concentrations of gaseous and particulate pollutants. MODIS observations highlight this important particulate pollution episode with AOT (550 nm) above 1 over large areas and values up to 4 along the intense fire plume transported in the anticyclonic flow. The model is able to reproduce the main aerosol plume features in terms of transport (spatial correlation of 0.4–0.8) and intensity (normalized mean bias of -(15–40 %)) during this specific period. The altitude of transport was shown to be below 5 km and comparisons between CHIMERE and CALIOP show good consistency. A large enhancement of the particulate pollution is detected over Moscow when the plume overpasses the area, with an AERONET

AOT (440 nm) from 0.56 on 5 August to 2–4 between 6 and 10 August. CHIMERE simulates rather well the temporal evolution of the AOT over Moscow during this period with biases from -53 % to 8 %, except for the 6 and 10 August. For these two days, the model underestimation is of 60–75 % due to some model deficiencies in simulating the transport of the intense aerosol plume over Moscow. Organics species are the dominant part of the aerosol composition simulated by CHIMERE over this area due to large OC and VOC emissions (mainly from wildfires with also an anthropogenic contribution), which lead to high SSA modeled over Moscow throughout the period with values of 0.97 (between 300 nm and 1000 nm), in good agreement with AERONET measurements over Moscow (0.95–0.96 between 440 nm and 1020 nm).

The impact of aerosols on photolysis rates is shown to be regionally significant with a mean reduction of J[NO_2] and J[O_3] comprised between 2 % and 50 %, the maximum reduction being modelled in the aerosol plume. These modifications of photolysis frequencies result in an regional increase in the daytime concentration of NO_2 of 3–15 % and a decrease in the O_3 production near the surface comprised between 1 % and 12 % during 8 August.

The photochemistry over the Moscow region has also been affected, especially during the arrival of the aerosol plume between 6 and 10 August 2010. Over this area, results indicate that J[O_3] is more sensitive to the presence of particles (reduction of about 10 % per unit of AOT) than J[NO_2] (reduction of about 6 % per unit of AOT), resulting in an increase of the ground NO_2 concentration of 3 % (per unit of AOT) and a small reduction of ozone of 1 % (per unit of AOT). The photochemistry is shown to be impacted along the boundary layer where aerosols are located with, for example, a 4–5 % O_3 reduction modelled during 9 August within the first two km of the atmosphere.

In addition, the impact of aerosols on photolysis rates is shown to have an influence on the formation of secondary aerosols, through the modification of the OH concentration. Over Moscow, the aerosol plume tends to decrease the daytime concentrations of sulphates and secondary organics up to 4–10 %, which result in a small reduction of the total particulate concentration (PM10) of 1–2 % on average over the period.

The results presented in this work, issued from a modelling exercise, are consistent with those obtained in recent studies by combining model experiments and different sets of observations. In terms of model performance, comparisons of simulations with air quality measurements at Moscow indicate that an explicit representation of aerosols interaction with photolysis rates tend to improve the estimation of the near-surface concentration of ozone and nitrogen dioxide as well as the formation of inorganic aerosol species such as ammonium, nitrates and sulphates.

Recently, it has been suggested that some organic aerosols can absorb solar radiation, especially at the shorter visible and UV wavelengths (Zhong and Jang, 2011; Saleh et al., 2014). The methodology developed in this study provides a powerful tool to investigate the role of enhanced UV absorption by secondary organics on photochemistry at regional and urban scale.

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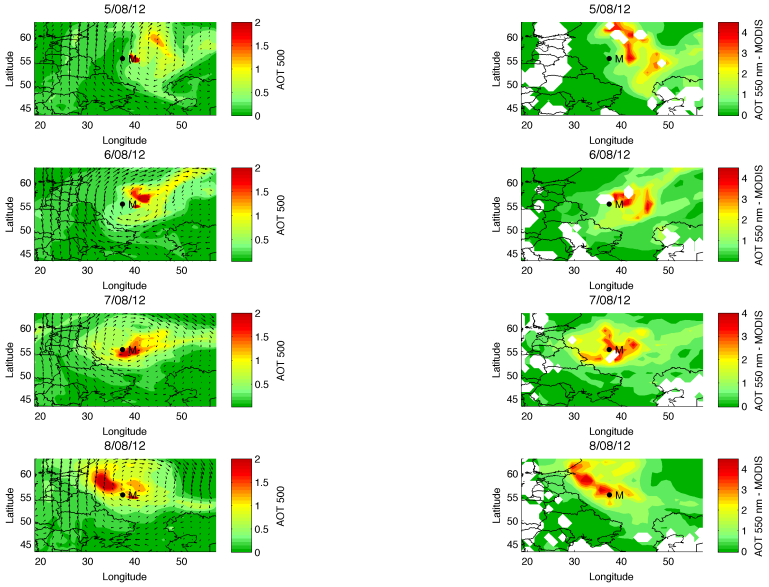

Fig. 1a. Geographic distribution of the AOT between 5 and 12 August 2010 modelled by CHIMERE at 500 nm (left panel) and measured by the Terra MODIS (Moderate Resolution Imaging Spectroradiometer) satellite sensor at 550 nm (right panel). The simulated 850 hPa wind is also indicated. M is the localization of Moscow and CFire and CnoFire are the localizations of the two CALIOP profiles used on figure 8

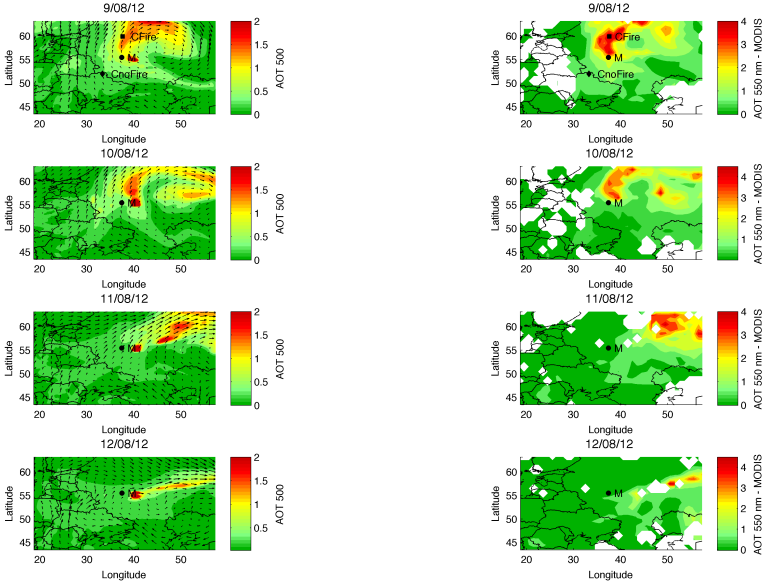

Fig. 1b. Continuation of Figure 1

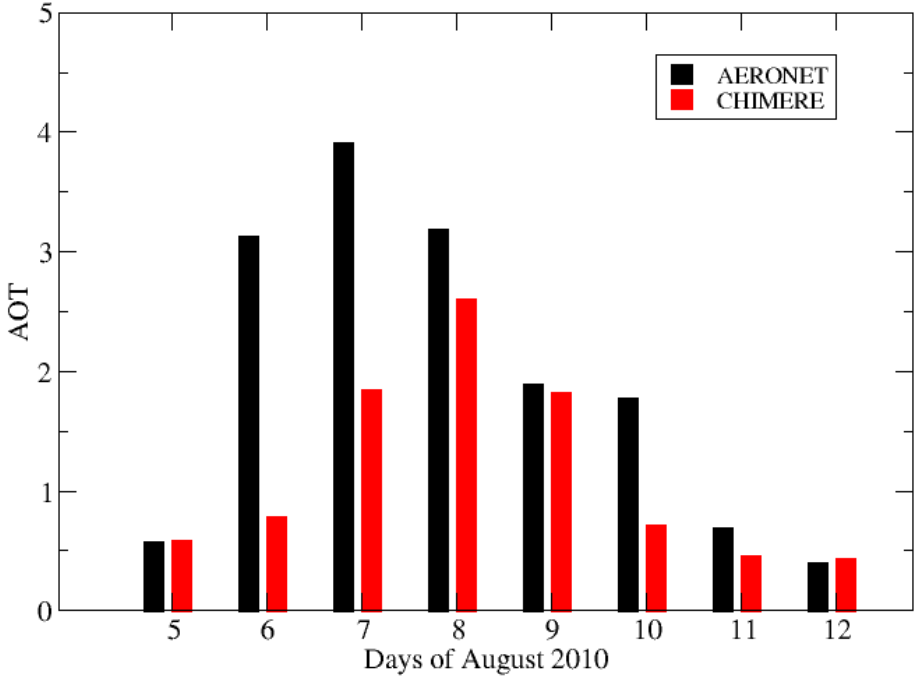

Fig. 2. Temporal evolution of the daily mean AOT over Moscow modelled by CHIMERE (at 400 nm) and measured by AERONET (at 440 nm) between 5 and 12 August 2010

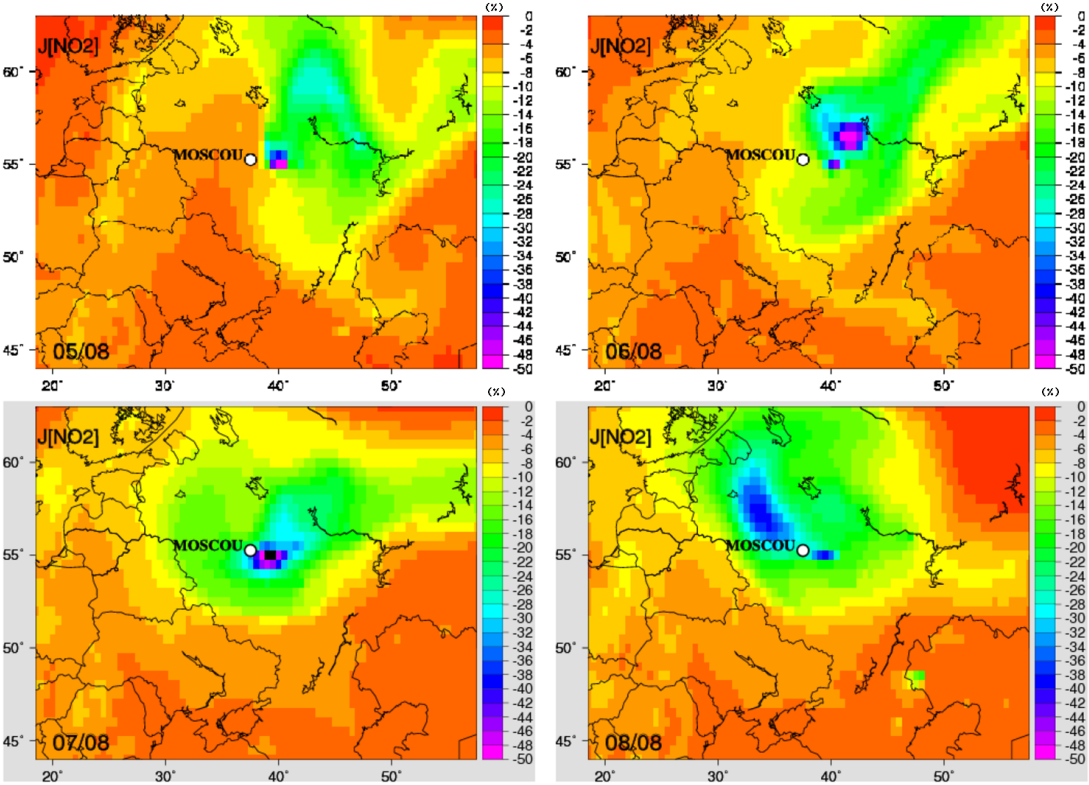

Fig. 3a. Geographic distribution of the modelled daytime average percentage changes in the near-surface J[NO_2] due to the presence of aerosols.

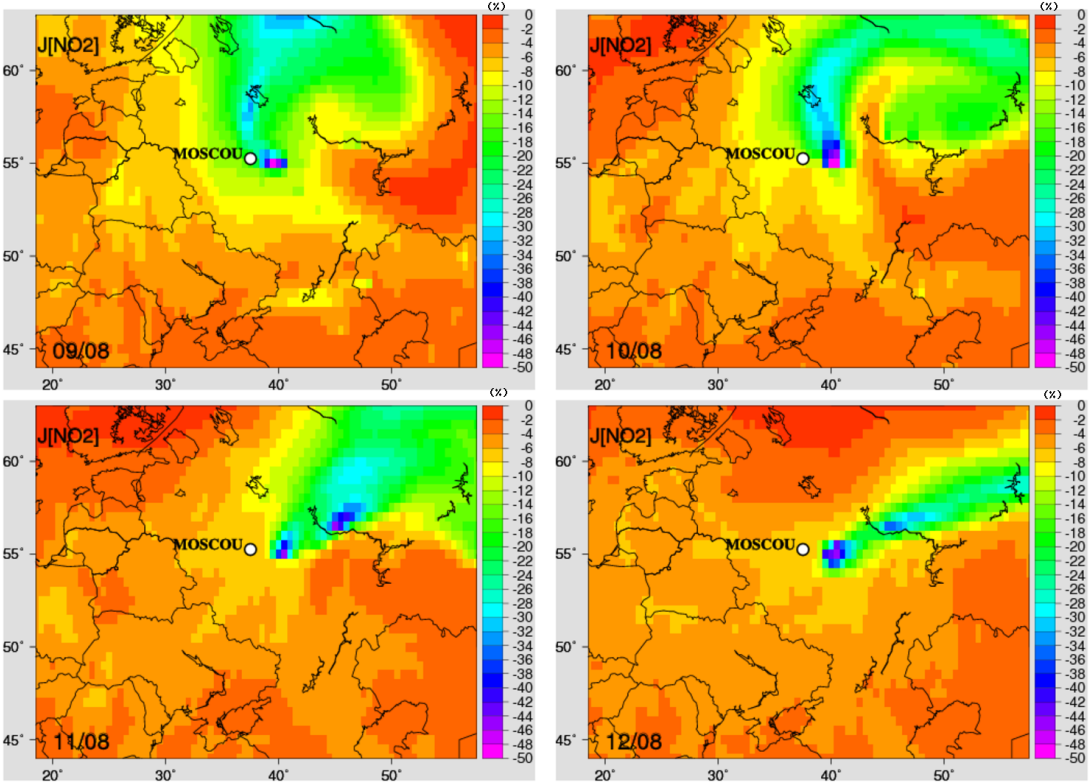

Fig. 3b. Continuation of Figure 3.

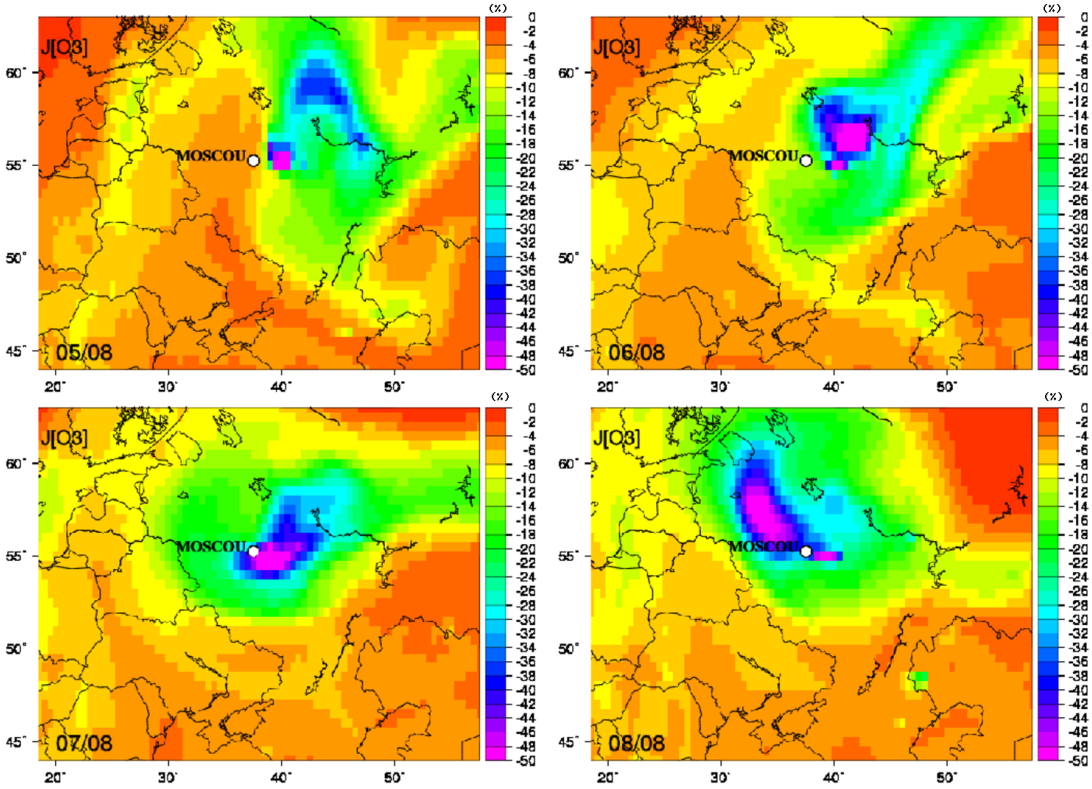

Fig. 4a. Geographic distribution of the modelled daytime average percentage changes in the near-surface J[O_3] due to the presence of aerosols.

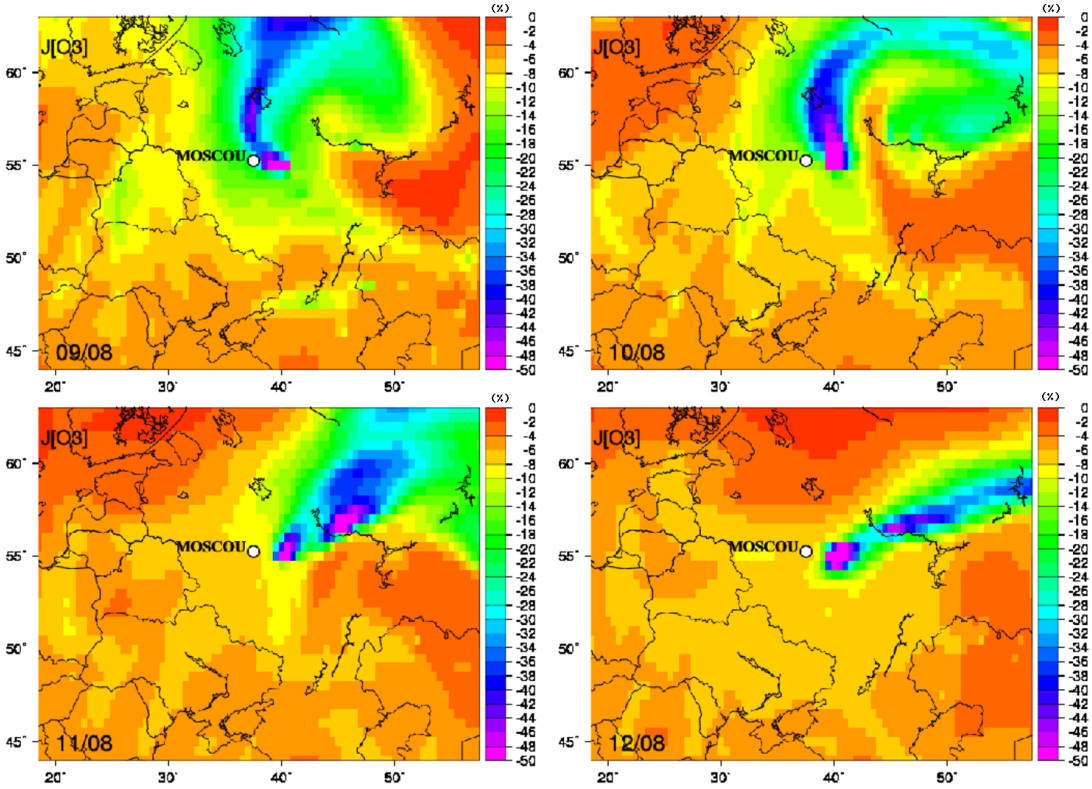

Fig. 4b. Continuation of Figure 4.

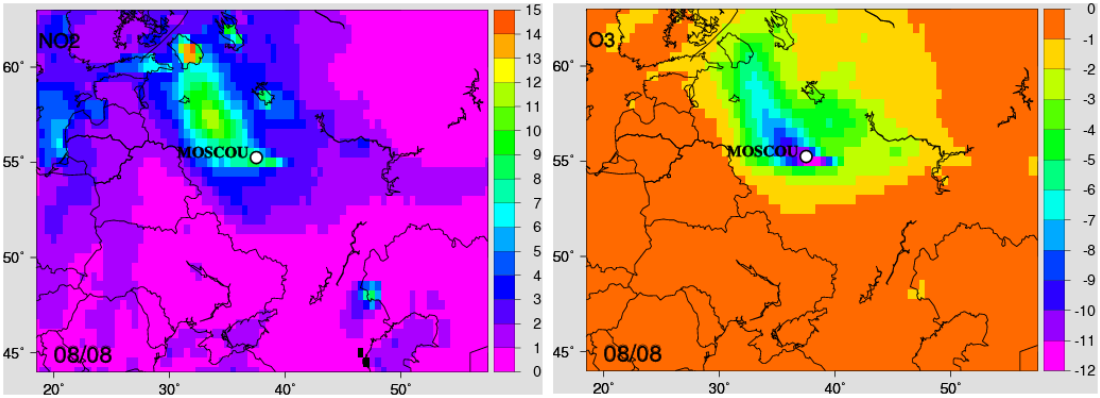

Fig. 5. Geographic distribution of the daytime average percentage changes in the near-surface concentration of NO_2 (left) and O_3 (right) for the 8 August 2010, due to the presence of aerosols.

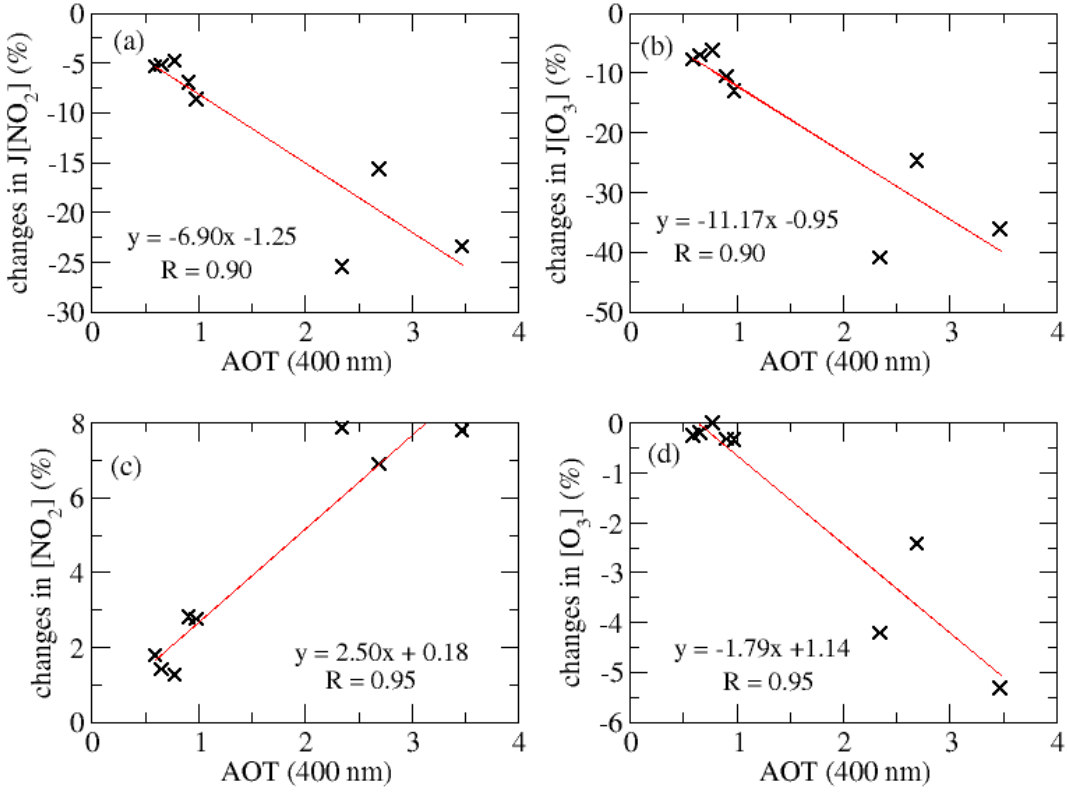

Fig. 6. Daytime average percentage changes in the photolysis frequencies and concentrations of nitrogen dioxide and ozone over Moscow as a function of modelled AOT (440 nm).

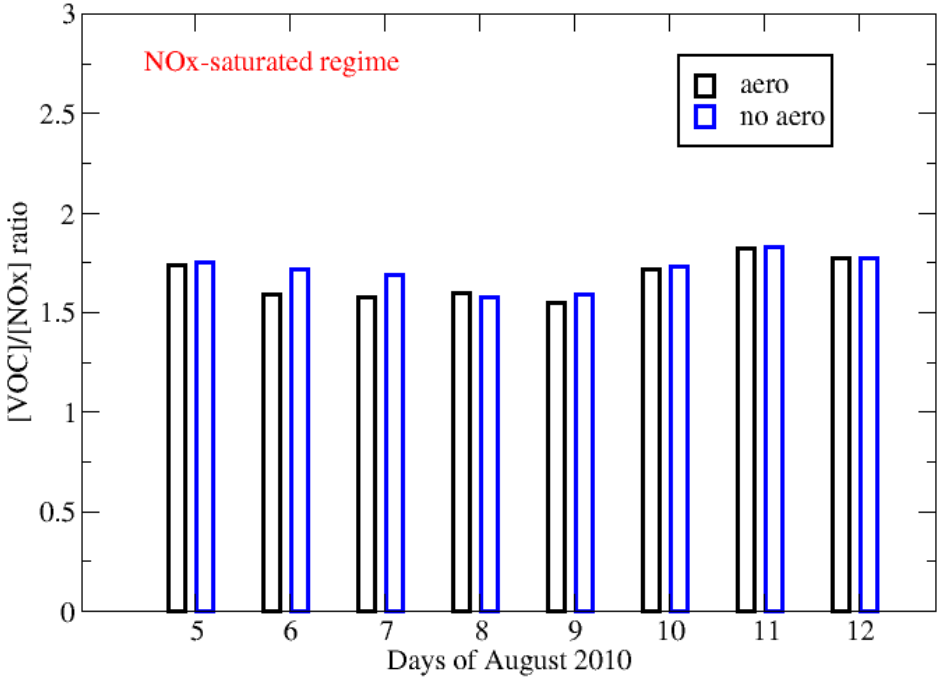

Fig. 7. Mean VOC(ppmC) to NOx(ppm) ratio simulated over Moscow during the studied period

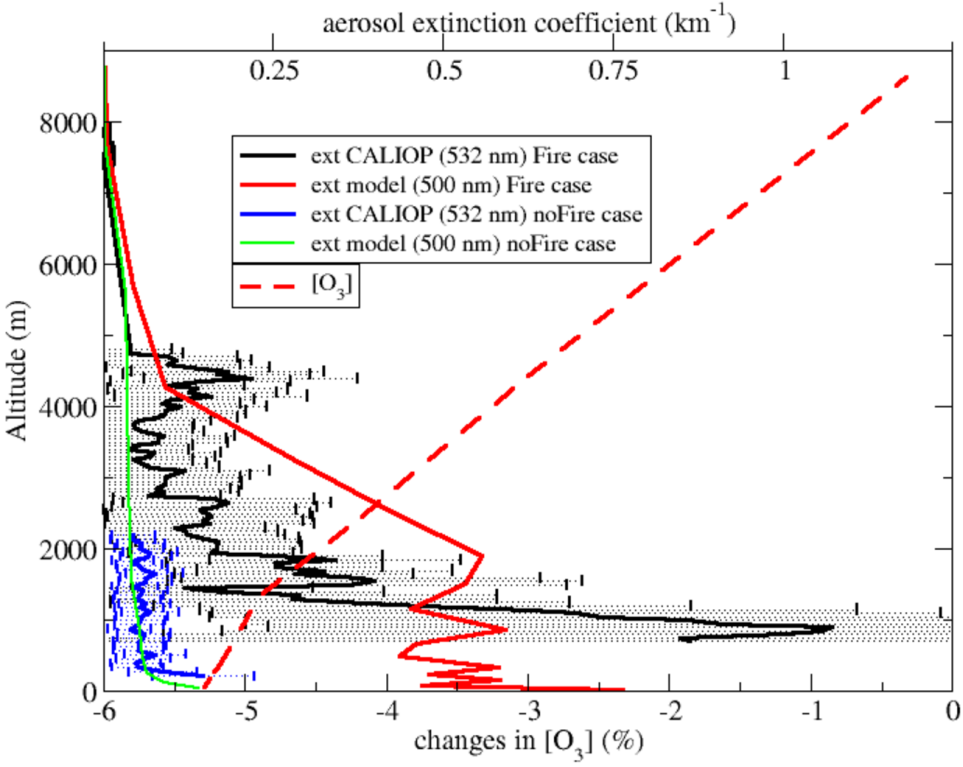

Fig. 8. The aerosol extinction coefficient (in km^{-1}) modelled by CHIMERE and measured by CALIOP for the 9 August inside (Fire case, 37.6 ^{o}E, 59.9 ^{o}N) and outside (noFire case, 33.3 ^{o}E, 52.0 ^{o}N) the intense aerosol plume (dotted lines correspond to the uncertainties on CALIOP measurements). The localisation of these two points is indicated on figure 1. The vertical profile of the daytime average percentage changes in the ozone concentration due to this intense aerosol plume is also indicated in red dashed line.

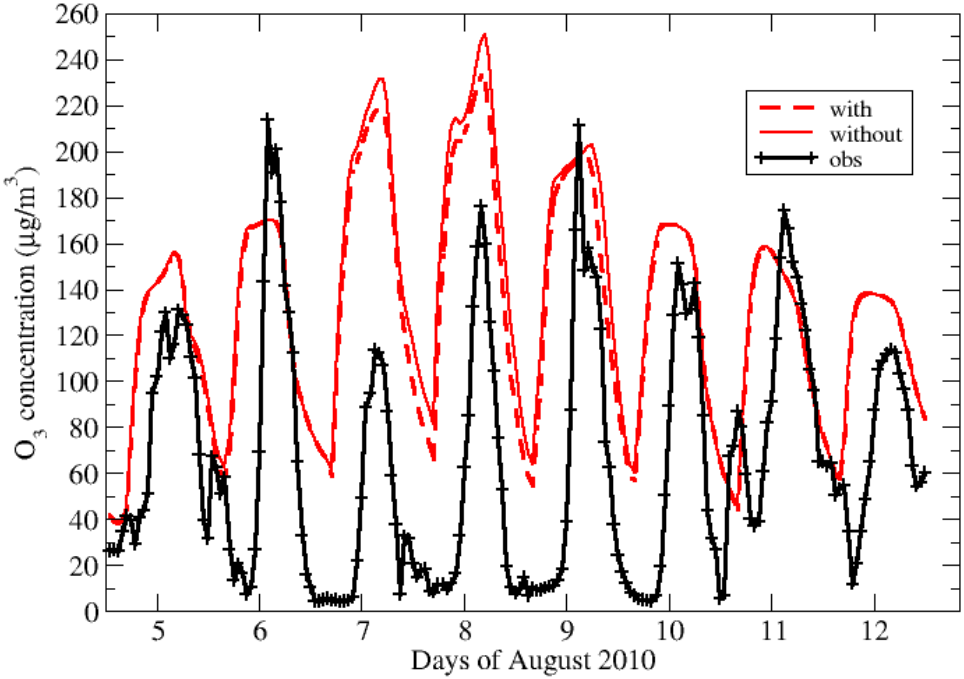

Fig. 9. Temporal evolution (between 5 and 12 August 2010) of the near-surface ozone concentration (in μg/m^3) modelled with and without aerosol feedback along with corresponding observations at the Moscow monitoring station.

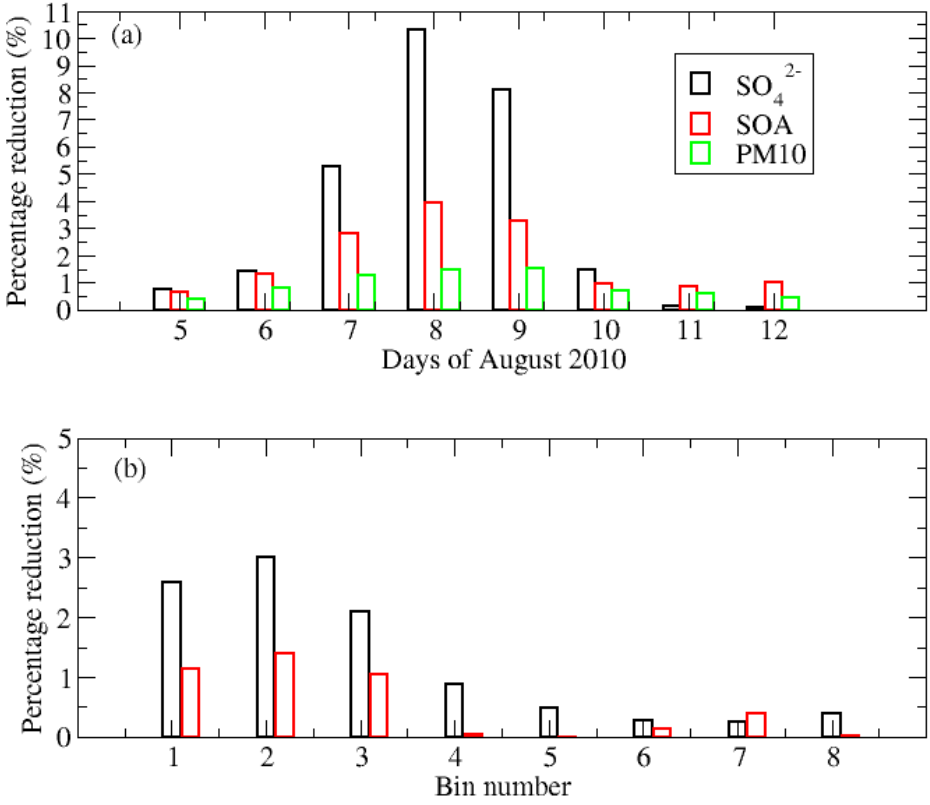

Fig. 10. a) Daytime average percentage reduction of the near-surface concentration of sulphates, secondary organic aerosols and PM10 over Moscow due to the aerosol feedback. b) Repartition of this sulphate and SOA mass reduction between the 8 aerosol size bins for the 8 August

Table 1. statistical comparisons between the near-surface concentrations of NO_2 and O_3 simulated with and without aerosols and measured at Moscow by an air quality station.
Mod. and Obs. are the period-averaged modelled and observed concentration. Corr. and RMSE are the temporal correlation and the root mean square error.

	NO_2				O_3			
	Mod. (μg/m^3)	Obs. (μg/m^3)	Corr.	RMSE (μg/m^3)	Mod. (μg/m^3)	Obs. (μg/m^3)	Corr.	RMSE (μg/m^3)
with	14	70	0.22	66	129	66	0.46	82
without	13	70	0.21	67	134	66	0.42	88

Table 2. Same as in Table 1 but for daily maximum values

	NO_2				O_3			
	Mod. (μg/m^3)	Obs. (μg/m^3)	Corr.	RMSE (μg/m^3)	Mod. (μg/m^3)	Obs. (μg/m^3)	Corr.	RMSE (μg/m^3)
with	32	90	0.60	66	180	161	0.19	48
without	31	90	0.60	67	185	161	0.16	54

Table 3. Same as in Table 1 but for the near-surface concentrations of ammonium, nitrates and sulphates. Measurements come from the Danki EMEP station RU0018R (near Moscow) located at 54.9 N and 37.8 ^{o}E.

	NH_4^+				NO_3^-				SO_4^{2-}			
	Mod. (μg/m^3)	Obs. (μg/m^3)	Corr.	RMSE (μg/m^3)	Mod. (μg/m^3)	Obs. (μg/m^3)	Corr.	RMSE (μg/m^3)	Mod. (μg/m^3)	Obs. (μg/m^3)	Corr.	RMSE (μg/m^3)
with	1.09	0.86	0.48	1.03	0.14	0.12	0.20	0.15	2.24	0.48	0.23	1.80
without	1.16	0.86	0.42	1.04	0.19	0.12	0.26	0.23	2.33	0.48	0.45	1.88