Long-term MAX-DOAS NO_2 measurements over Athens and association with urban sources

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Data and methodology

MAX-DOAS measurements

The MAX-DOAS instrument is performing measurements at 527 m a.s.l. (Gratsea et al., 2016). It is located in Penteli (30.05ºN, 23.86ºE), at the premises of the National Observatory of Athens and is part of the BREDOM network (Bremian DOAS network for atmospheric measurements) (Wittrock et al., 2004). It performs measurements of scattered sunlight at the UV-vis range; a rotating telescope points at eight azimuthal angles and at nine elevation angles (-1º, 0 º, +1º, +2º, +4º, +8º, +15º, +30º and zenith). At low elevation angles the light path through the troposphere is much longer (-> higher sensitivity to near-surface absorbers). The duration of one cycle through all the directions is about 15 minutes. No strong emission sources are present around the measurement area.

The DOAS (Differential Optical Absorption Spectroscopy) technique is a remote sensing technique for the retrieval of trace gases columns from diffuse solar radiation measurements (Platt and Stutz, 2008). For this study, NO_2 tropospheric slant column densities (DSCDs) were retrieved for the period October 2012 - July 2017.

Fig. 1: MAX-DOAS location and viewing directions over Athens

In situ measurements

Surface NO_2 hourly concentrations for this study were obtained from chemiluminescence measurements performed at three monitoring stations of the National Network for Atmospheric Pollution. Two stations (PAT and SMY) are characterised as urban and urban background, respectively, and coincide with the MAX-DOAS urban direction and one (KOR) is characterized as suburban and coincide with the remote direction

Model predictions

The simulations of reactive pollutants on the city scale is performed by the EPISODE-CityChem Chemistry Transport Model (Karl et al., 2019; Hamer et al., 2019). The model is applied for a domain over Athens (SW corner: 23.4E°, 37.8N°); (45×45 cells of 1×1km²), with an embedded receptor grid 100×100m²) for a winter and a summer month of 2016 (Fig. 3). Boundary AQ and emission inputs are derived from Copernicus. The meteorological data was retrieved from ECMWF ERA5 through TAPM (Hurley, 2008).

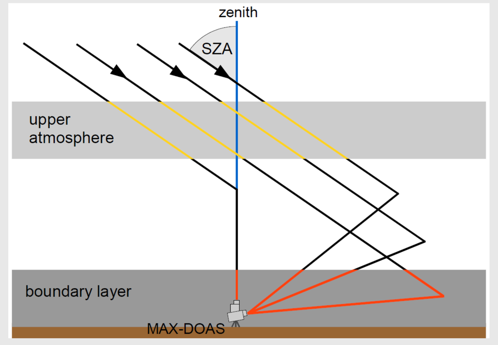

Fig. 2: Schematic overview of the observation geometries

Contribution of urban sources

As a further insight to the contribution of the NO_2 urban sources, the $DSCD_{NO2}$ levels over the remote area were subtracted from the urban measurements for two months: Jan 16 (winter conditions) and Jun 16 (summer conditions).

- The contribution of the urban sources (mainly traffic emissions) to the urban pollution was found **35%** and **65%** for January and June, respectively. This difference is expected due to high temperatures and intense photochemistry during summer, when in presence of high NO emissions, the photochemically produced ozone leads to more intense conversion of emitted NO to NO_2.

- The simulations of the city-scale model showed that over the urban center of Athens most of this fraction (**20-35%**) is due to road transport, which does not vary between January to June, according to the specific set of simulations.

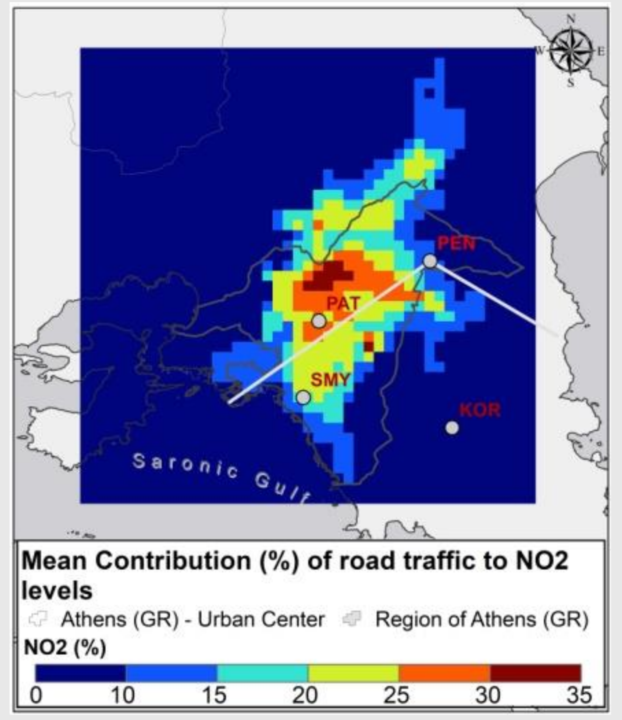

Fig. 3: The model domain for the current simulations of air pollution in Athens. The three in situ monitoring stations (PAT, SMY and KOR) and the location of MAX-DOAS (PEN) are indicated, as well as the two azimuthal viewing directions of MAX-DOAS (white lines). Contours show the contribution (%) of road traffic to NO_2 concentration values, averaged for the whole simulation period.

Vertical distribution of diurnal cycles

- The winter and summer hourly averages for the 5-year period reproduce well the morning traffic rush hours for Athens, peaking at 10:00LT. The results are in agreement with other studies showing that the rush hours in Athens are from 08:00 LT until 11:00 LT (e.g. Kourtidis et al., 1999).

- The difference of an order of magnitude between the +1º and the +30º elevation angles can serve as a confirmation of the assumption that the absorption by NO_2 in the boundary layer dominates the retrieved tropospheric signal in the polluted urban environment. Hence, in the presence of high levels of NO_2 in the lower troposphere, the SC densities are strongly decreasing with increasing elevation angle (Hönninger et al., 2004).

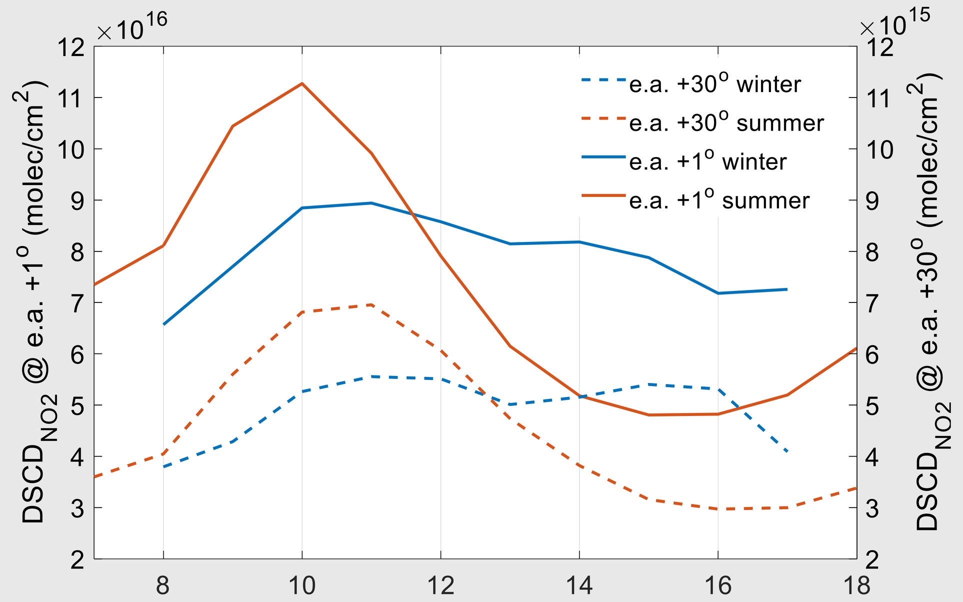

Fig. 4: Hourly averages in LT for winter (blue curves) and summer (red curves). Solid and dashed lines correspond to measurements at the +1º and +30º elevation angles, respectively.

Comparison with in-situ NO_2 measurements

Range of MAX-DOAS measurements

Lower elevations have vertical sensitivity curves that peak towards the surface, which makes them more sensitive to NO_2 in the boundary layer, and which give them a larger horizontal domain of representativity (typically 5 km, depending on aerosol conditions). Therefore, the comparison with the in situ measurements was carried out using MAX-DOAS data from the +1º elevation angle.

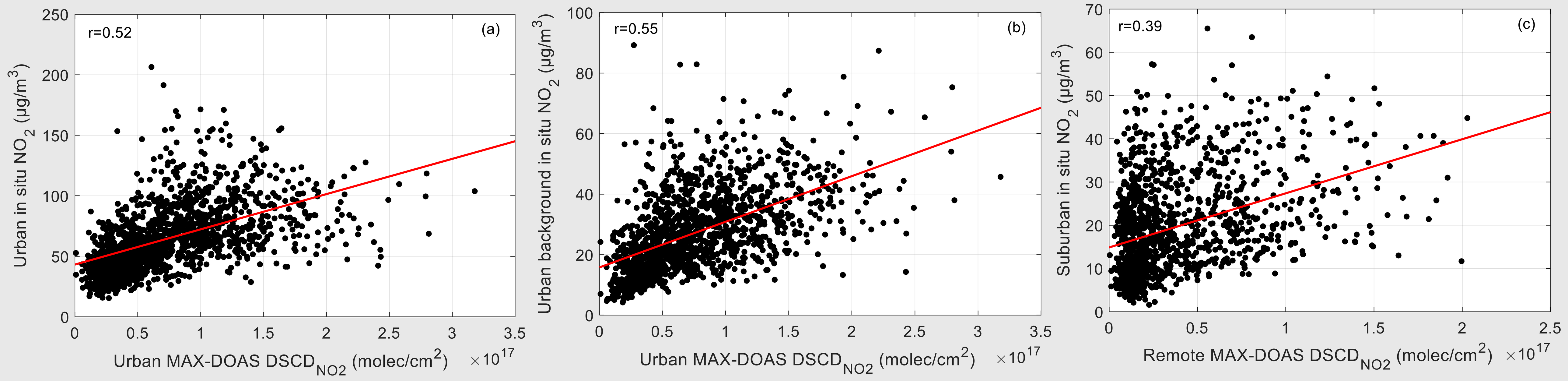

Fig. 5: Daily averaged MAX-DOAS retrieved NO_2 differential slant column densities (DSCDs) and NO_2 concentrations from the three in situ monitoring stations; (a) urban, (b) urban background and (c) suburban. Period: October 2012 to September 2017.

- Moderate correlation: r≈0.55 and 0.40 for the urban and remote area, respectively
- In some cases, in situ instruments measure a strong NO_2 signal even when MAX-DOAS is measuring low values. This would be expected, as the monitoring stations measure NO_2 near to the surface, whereas the MAX-DOAS measures NO_2 throughout the boundary layer.

The two observation techniques yield different samplings of the atmosphere on a spatial scale, which can introduce biases.

Seasonality and spatial aspects

- Seasonal variation demonstrates the expected seasonal characteristics, with lower concentrations in summer due to decreased anthropogenic emissions and high photolysis rate, and enhanced concentrations during winter due to increased emissions (residential heating and traffic).
- Both measurement techniques show a 50% decrease of NO_2 in the remote area, all year long.
- Very good correlation (r=0.86) between the urban direction of MAX-DOAS and the urban background in-situ station is found, suggesting that the MAX-DOAS can provide reliable information on NO_2 variation in the air masses over the city.

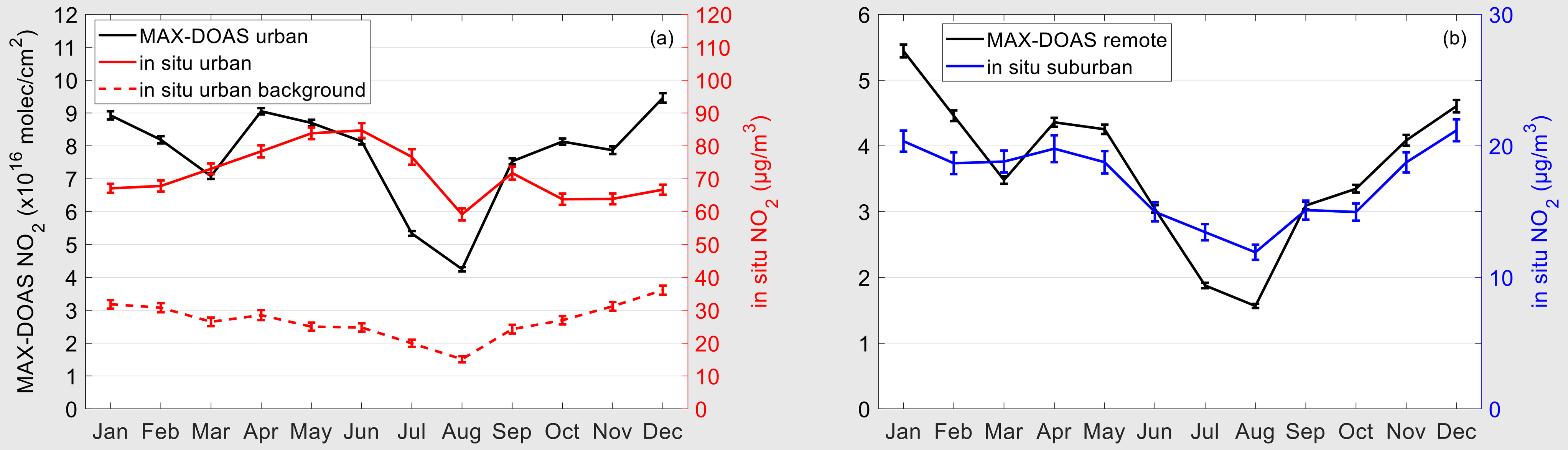

Fig.6: NO_2 monthly averages for the period October 2012 - September 2017 for the urban (left panel) and the remote area (right panel).

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