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NO_2 AND SO_2 OBSERVATIONS IN SOUTHEAST EUROPE USING MOBILE DOAS OBSERVATIONS

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Abstract: In this work we present the first and longest zenith-sky mobile DOAS (Differential Optical Absorption Spectroscopy) measurements performed in Southeast Europe. The mobile DOAS observations were performed on board of a motor vehicle using an UV-Vis spectrometer during several days on 2015 and 2016 in Romania, Bulgaria, Greece and Republic of Moldova. The target trace gases are: nitrogen dioxide (NO_2) and sulfur dioxide (SO_2). The mobile DOAS measurements performed on ground represents aproximative 1500km travelled on roads. The highest tropospheric NO_2 ($1x10^{17}$ molec./cm^2) and SO_2 ($\sim 2.5x10^{18}$ molec/cm^2) content was determined in the Jiu Valley Romania, where large fossil-fuel power station exist. The study also presents comparisons of tropospheric NO_2 Vertical Column Density (VCD) deduced from mobile DOAS measurements with Ozone Monitoring Instrument observations. We found a good agreement between ground and space observations for two important urban agglomerations. For Bucuresti city the averaged mobile DOAS observations function of OMI pixel coordinates show 4.11 (±0.61) $x10^{15}$ molec/cm^2 while OMI detected 5.94 (±2.87) $x10^{15}$ molec/cm^2. For the other important city, Thessaloniki, averaged mobile DOAS observations indicate 5.44 ± (0.84) $x10^{15}$ molec/cm^2 while OMI space observations presents 5.66 (±1.56) $x10^{15}$ molec/cm^2. We found also that due to the smoothing effect inside the pixel, OMI sensor underestimated the important NO_2 emissions located in the Jiu Valley, Romania.

Keywords: atmosphere, nitrogen dioxide, sulfur dioxide, mobile DOAS observations, space observations

1. INTRODUCTION

Nitrogen dioxide (NO_2) and sulphur dioxide (SO_2) are trace gases with an important impact on the Earth's atmosphere. The main anthropogenic sources of NO_2 and SO_2 are related to the combustion of fossil fuels from industry and transport, while the natural emissions sources are lightning and microbial activity in soil for NO_2, respective volcanoes for SO_2. NO_2 and SO_2 in the atmospheric boundary layer have short lifetimes (in summer less then 1 day) being located nearby their emissions sources (Krotkov et al., 2016). NO_2 and SO_2 are known as toxic trace gases which in high concentrations can be harmful for vegetation and human health (Chen et al., 2007).

The Differential Optical Absorption Spectroscopy (DOAS) technique (Platt & Stutz, 2008) is a well established method that has been successfully used for the NO_2 and SO_2 monitoring from ground and space. The ground-based DOAS observations can be static or mobile. The static observations are represented by ground based zenith-sky (Tack et al., 2015) or Multi Axis (MAX)-DOAS observations (Hendrick et al., 2014). The mobile DOAS observations can be performed onboard of multiple platforms. The space DOAS observations performed on board of satellites (Burrows et al., 1999; Bovensmann et al., 1999; Levelt et al., 2006) can be included in the category of mobile DOAS observations. Others platforms used for mobile DOAS observations are: motor vehicles (Constantin et al., 2013a), ships (Schreier et al., 2015), balloons (Strong et al., 2005), airplanes

(Merlaud et al., 2012) and UAV –Unmanned Aerial Vehicles (Merlaud et al., 2014).

During the last two decades the variability of NO_2 and SO_2 at global and regional level has changed. Studies using data from the space-borne sensor Ozone Monitoring Instrument confirmed an important reduction in NO_2 and SO_2 over Eastern Europe, North China and USA (Krotkov et al., 2016; Constantin et al., 2013b) while an increasing trend in NO_2 and SO_2 was observed over India and the Persian Gulf (Krotkov et al., 2016).

In this work, we present measurements of NO_2 and SO_2 using zenith-sky mobile DOAS observations performed in Southeast Europe. In the next section, we describe the Methodology. In Section 3 we introduce the Results and Discussions followed by Conclusions.

2. METHODOLOGY

Nowadays the DOAS technique is an often method which is used on a regular basis to determine the trace gases of the atmosphere.

The zenith-sky mobile DOAS technique is able to detect the scattered sunlight under the zenith angle over different areas where the mobile platform is able to go. In this work we present zenith-sky mobile DOAS observations performed in Southeast Europe using a motor vehicle. The measurements were performed during 2015-2016 in Romania, Republic of Moldova, Bulgaria and Greece (see Fig. 1 and Table 1).

Table 1. Temporal and spatial coverage of mobile measurements

Country	Day	Route	Distance traveled
Bulgaria	19 May 2016	Granichar-Varna	100km
Greece	22 March 2016	Agia triada-Alexandroupolis	330km
Romania	24 iunie 2015	Craiova-Rovinari	90km
	01 May 2016	Sebes-Slobozia	470km
	19 May 2016	Galati-Vama veche	300km
Moldova	05 September 2015	Sarata galbena-Cricova	70km

NO_2 and SO_2 atmospheric content was measured using a mobile DOAS instrument which consists mainly in a compact UV-Vis spectrometer (AvaSpec-ULS2048XL), computer, telescope, optical fiber and a GPS antenna. A sketch of the mobile DOAS system used in this study is presented in figure 2.

Figure 1. The route of mobile DOAS measurements in Southeast Europe (black lines)

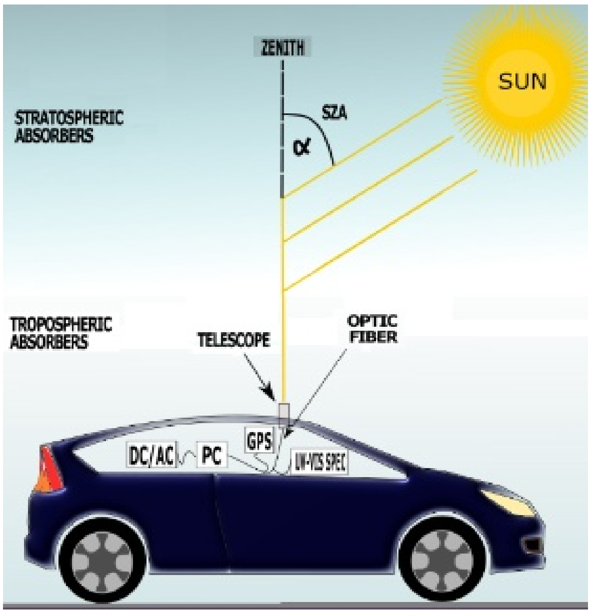

Figure 2. The mobile DOAS system

More details about the zenith-sky mobile DOAS system can be found in Constantin et al., 2013a. The zenith-sky spectra presented in this study were analyzed using the QDOAS software (Danckaert et al., 2014), developed at BIRA-IASB. The output of the QDOAS spectral analisys is a Differential Slant Column Density (DSCD). The differential absorption cross sections used in this study are SO_2 (294 K), O_3 (223 K; 243 K), NO_2 (298 K), H_2O (296 K) and O_4 (293 K). Also a synthetic Ring spectrum was included in the DOAS fitting. A five-order polynomial was used as fitting parameters to determine the DSCDs of NO_2 respective SO_2. The laboratory cross sections used for the fitting of NO_2 and respective SO_2 are presented in table 2.

All the zenith-sky mobile DOAS observations presented in this work were performed under clear or mostly clear sky conditions. Inconsistent data caused by the occasional obstruction of the field of view (e.g. trees, tunels, etc) or others instabilities were filtered out using the fitting Root Mean Square (RMS) and the O_4 also known as the collisional complex of $(O_2)_2$.

The tropospheric NO_2 and SO_2 vertical column density (VCD) determined from mobile zenith-sky observations was calculated using the retrieval algorithm presented by Constantin et al., 2013a. The NO_2 retrieval algorithm is based on OMI space observations beside DOAS static twilight observations performed on July 2015. More details about the NO_2 retrieval algorithm can be found in Constantin et al., (2013a). The atmospheric SO_2 content will be presented as a DSCD.

3 RESULTS AND DISCUSSIONS

3.1 Tropospheric NO_2 & SO_2 in Southeast Europe

Figures 3 and 4 presents the time series plot of NO_2 DSCDs and VCD_{tropo} calculated from the zenith-sky spectra recorded on June 2015 nearby the Romanian power plants Craiova, Isalnita, Turceni and Rovinari. All these power plants are located in the Jiu Valley. These power plants represent one of the largest electricity generation complex from Southeast Europe. Another important electricity generation complex can be found in Bulgaria, Maritsa Iztok Complex, however the mobile DOAS measurements were performed on May 19th, 2016 in Bulgaria were not aimed to measure the NO_2 and SO_2 plume emited by the industrial sources from this country. In Romania, the highest amount of tropospheric NO_2 (~$1x10^{17}$ molec/cm^2) was detected around the power plant located in Turceni. The NO_2 peak of was detected very close to the power plant, because, due to dispersion, the NO_2 concentration rapdidly decrease with the distance from the source. The same effect is visible also for the SO_2 observed by mobile DOAS technique in the same area (Fig. 4). The comparison between the two figures (NO_2 and SO_2) shows that the SO_2 peaks doesnot corespond to the NO_2 peaks. The main reason of this mismatch between NO_2 and SO_2 peaks is due to the SO_2 removal technologies used by the power plants under investigation (e.g. Isalnita power plant). In Romania, beside the large power plants whose emissions are clearly visible in satellite measurements (Constantin et al., 2013b), another important source is Bucuresti city.

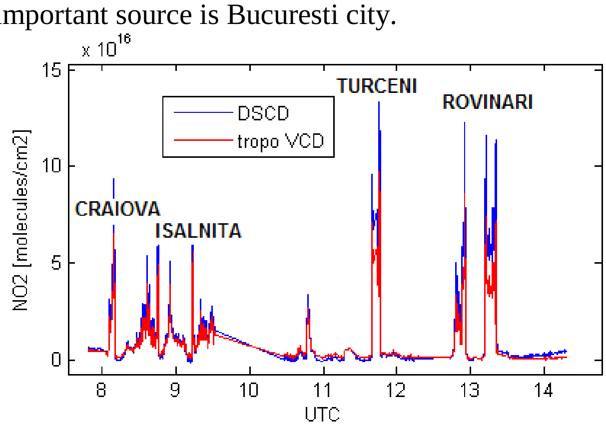

Figure 3. Time series of NO_2 DSCD and tropospheric NO_2 VCD column determined over the Jiu Valley on 24 June 2015

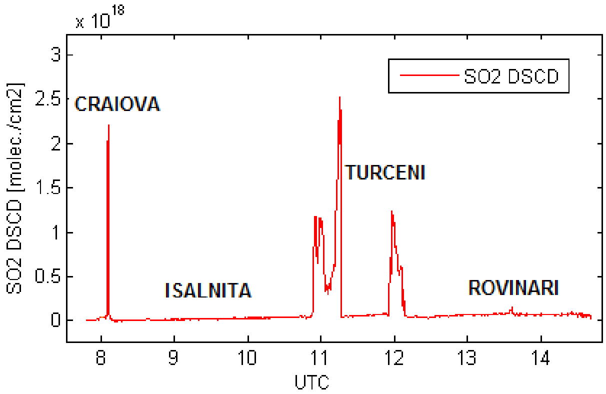

Figure 4. Time series of SO_2 DSCD determined over the Jiu Valley on 24 June 2015

Table 2. The settings used for NO_2 and SO_2 spectral fitting

	NO_2 – NITROGEN DIOXIDE	**SO_2** – SULFUR DIOXIDE
Wavelength range	425-490 nm	305– 325 nm
Polynomial degree	5	5
Intensity offset	constant	constant
Ring spectrum	NDSC Ring	yes
Trace gas cross sections	NO_2 298K (Vandaele et al., 1996) O_3 223K (Bogumil et al., 2003) Ring_NDSC2003.xs H_2O 296K (Rothman et al., 2010) O_4 293k (Thalman & Volkamer, 2013)	O_3 223K (Bogumil et al., 2003) SO_2 294K (Vandaele et al., 1994) Ring conv. O_3 243K (Bogumil et al., 2003)

The measurements performed on May 1st, 2016 around Bucuresti were done on the ring road of the city. A tropospheric NO_2 column with a max peak of ~$8x10^{15}$ molec./cm^2 was measured along the ring road. However May 1st, 2016, was a day off (Easter and Labor Day) and traffic and industrial activities were reduced. Satellite measurements show that Romania and Eastern Europe are regions with a relatively low level of NO_2 and SO_2. The level of NO_2 and SO_2 observed from space compared to the zenith-sky mobile DOAS will be presented in the next subsection.

3.2 Comparisons with satelitte observations

Space observations presented in this section are performed by OMI instrument. OMI is a nadir-viewing UV-Vis spectrometer designed to monitor atmospheric species and aerosols. OMI space instrument provides daily global observations at a spatial nadir resolution of 13 × 24 km². For NO_2 observations OMI has a very good detection.

The SO_2 level in Romania is under the detection limit of OMI (~0.2 DU), due to this reason OMI sensor can not detect the SO_2 loadings emitted by power plants (Krotkov et al., 2016), SO_2 amount which is observed very clear by mobile DOAS observations (Fig. 4). The SO_2 level in Romania has dramatically decreased over the last 20 years. For this reason OMI SO_2 maps are not presented in this paper. Nearby Craiova power plant the mobile DOAS instrument was able to detect a maximum SO_2 DSCD peak of ~$2.2x10^{18}$ molec/cm^2 and ~$2.5x10^{18}$ molec/cm^2 nearby Turceni. No important SO_2 amount was observed nearby Isalnita and Rovinari power plants, where SO_2 filters were installed.

Figures 5÷8 introduce the NO_2 color coded comparisons between mobile DOAS measurements and OMI observations for the measurements performed in Romania, Bulgaria, Greece and Moldova. The main cities encounterd during the mobile DOAS measurements and the NO_2 amount observed from space and ground are presented in Table 3. The ground mobile DOAS observations performed inside of an OMI pixels were averaged function of pixel corner coordinates. For important urban agglomerations (e.g. Bucuresti and Thessaloniki) OMI observations are consistent with mobile DOAS measurements. In the case of industrial locations (the Romanian power plants), OMI underestimate the ground observations. This underestimation comes from the smoothing effect inside the pixel, OMI pixel have a surface of 312km^2 while the NO_2 emissions from these sources are very localized.

Figure 5. Mobile DOAS measurements and OMI observations on 22 March 2016, in Greece

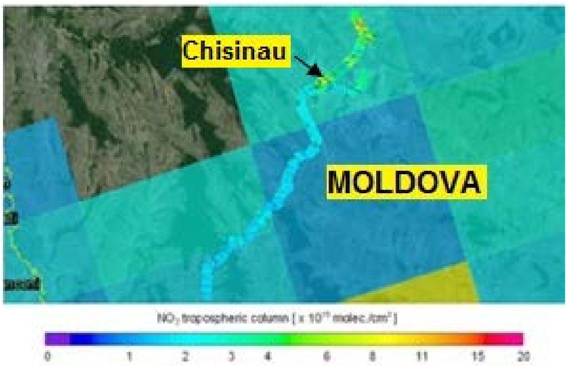

Figure 6. Mobile DOAS measurements and OMI observations on 05 September 2015, in Moldova

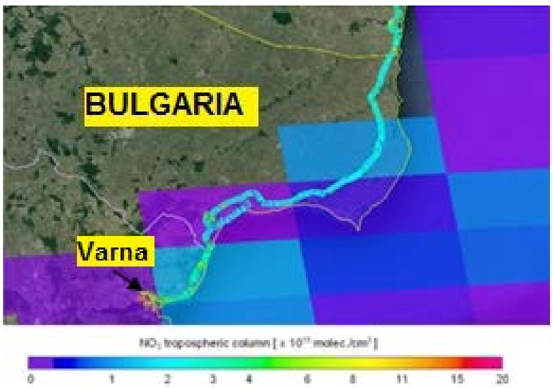

Figure 7. Mobile DOAS measurements and OMI observations on 19 May 2016, in Bulgaria

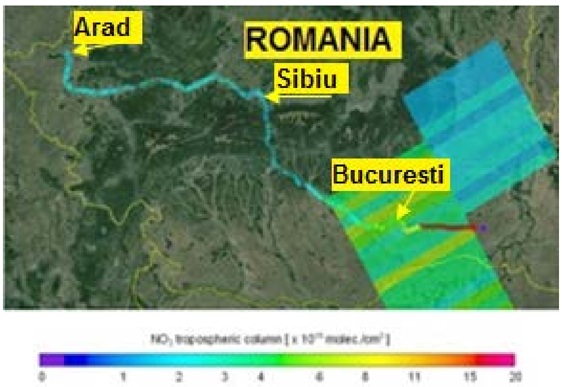

Figure 8. Mobile DOAS measurements and OMI observations on 1 May 2016, in Romania

Table 3. Tropospheric NO_2 VCD observed from ground and space DOAS observations.

City (country)	Day	tropoNO_2 VCD Average [x10^{15} molec./ cm^2]	Time interval Mobile DOAS [UTC]	NO_2 OMI pixel [x10^{15} molec./cm^2]	OMI Overpass time [UTC]
Arad (RO)*	01.05.2016	2.12(±0.42)	8.30-8.58	n/a	n/a
Braila (RO)	19.05.2016	12.6(±0.26)	7.60-8.05	1.62(±0.95)	11.61
Bucuresti (RO)	01.05.2016	4.11(±0.61)	15.81-16.53	5.94(±2.87)	10.26
Constanta (RO)	19.05.2016	6.02(±1.21)	10.28-10.41	1.21(±0.88)	11.61
Craiova (RO)	24.06.2015	23.4(±4.4)	7.91-8.23	2.95(±0.95)	11.01
Galati (RO)	19.05.2016	10.3(±2.74)	6.88-7.51	0.86(±0.75)	11.61
Isalnita (RO)	24.06.2015	10.9(±3.45)	8.39-9.51	2.95(±0.95)	11.01
Pitesti (RO) *	01.05.2016	2.09(±0.49)	14.8-14.97	n/a	n/a
Rovinari (RO)	24.06.2015	15.4(±3.56).	12.72-13.55	3.0(±1.24)	11.01
Sebes (RO) *	01.05.2016	3.11(±0.77)	11.41-11.81	n/a	n/a
Sibiu (RO) *	01.05.2016	1.69(±0.34)	12.37-12.48	n/a	n/a
Turceni (RO)	24.06.2015	15.4(±2.77)	10.50-12.01	2.65(±0.95)	11.05
Chisinau (MD)	05.09.2015	3.43(±0.68)	13.84-14.06	1.56(±0.64)	10.99
Albena(BG)	19.05.2016	3.30(±0.59)	13.84-13.91	0.05(±0.95)	11.61
Varna (BG)	19.05.2016	5.82(±1.37)	15.81-16.53	2.14(±1.58)	11.61
Alexandroupoli(GR)*	22.03.2016	0.92(±0.24)	16.29-16.42	n/a	11.01
Kavala (GR) *	22.03.2016	0.78(±0.13)	14.67-14.81	n/a	11.01
Komotini (GR) *	22.03.2016	1.23(±0.19)	15.55-15.79	n/a	11.01
Thessaloniki (GR)	22.03.2016	5.44(±0.84)	13.21-13.45	5.66(±1.56)	11.01

* For this city the average of the mobile DOAS observation was done according to the city limits

4. CONCLUSIONS

In this work we presented the first and longest zenith-sky mobile DOAS observations performed in Southeast Europe (Romania, Bugaria, Greece and Moldova). The mobile DOAS observations were performed during 2015-2016. The aim of the remote sensing observations was to determine the spatial distribution of NO_2 and SO_2 over or nearby important locations in Southeast Europe (e.g. Bucuresti, Chisinau, Thessaloniki, Varna, etc). During the mobile DOAS observations an important tropospheric SO_2 amount was detected on the Jiu Valley Romania, where large fired coal power plants exist. We observed at the power plants that have implementd SO_2 removal technologies that no imporant SO_2 amount was detected. A SO_2 peak of ~2.5x10^{18} molec/cm^2 was detected nearby Craiova and Turceni power plants. Comparisons between mobile DOAS measurements and OMI space observations were presented. We found a good agreement between ground and space observations for the urban agglomerations Bucuresti and Thessaloniki. On 1st of May 2016 over Bucuresti city OMI detected 5.94(±2.87) x10^{15} molec/cm^2 while ground DOAS observations shows 4.11(±) x10^{15} molec/cm^2; for Thessaloniki city OMI detected 5.66(±1.56) x10^{15} molec/cm^2 and ground DOAS shows 5.44±(0.84) x10^{15} molec/cm^2. We found also that OMI sensor understemited the important NO_2 sources located in the Jiu Valley, Romania; e.g. on 24 June 2016 the OMI pixel located over Turceni presents a NO_2 loading of 2.65(±0.95) x10^{15} molec/cm^2 while the mobile DOAS observations averaged according to the space foot print shows 15.4(±3.56)x10^{15} molec/cm^2. A similar inconsistency was observed also for Craiova, Isalnita and Rovinari, locations where fired coal power plants exists.

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