~~An~~Effects of urban agglomeration ~~effect~~ on surface UV doses: ~~Comparison~~a comparison of ~~the~~ Brewer measurements in Warsaw and ~~at~~ Belsk, Poland, for the period 2013-2015

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Abstract. ~~The specific~~Specific aerosols and cloud properties over large urban regions seem to generate an island, similar to the well-~~know~~known city heat island, leading to lower UV radiation intensity compared to the surrounding ~~cleaner~~less polluted areas, thus creating a shield against excessive human exposure to ~~the~~ UV radiation. The present study focuses on differences ~~in the~~between erythemal and UV-~~A1 (340-400~~A (324 nm) doses measured by the Brewer spectrophotometers in Warsaw (52.3ºN, 21.0ºE) and ~~at~~ Belsk (51.8ºN, 20.8ºE~~), which~~). The latter is ~~located in~~ a rural region ~~at a distance of~~ located about 60 km ~~in the~~ south-west ~~direction from~~ of the city. ~~The ratio~~Ratios between erythemal and UV-~~A1~~A partly daily doses, obtained during all-sky and cloudless-sky conditions ~~in~~for the period May 2013-December 2015, ~~are analyzed~~were analysed to infer a specific cloud and aerosol forcing on the surface UV doses over Warsaw. Radiative model simulations ~~are~~were carried out to ~~assess impact~~find sources of the ~~Warsaw-Belsk~~observed differences ~~in total ozone, geographical location and albedo, on the mean ratio between the doses. Higher surface albedo over the city compensates the effect of solar elevation differences due to latitude differences as the mean total ozone values appear almost the same over both~~ between the sites. It ~~is~~was found that Warsaw urban agglomeration induced 8% and ~~5~~6% attenuation of the erythemal and UV-~~A1~~A doses, respectively, ~~which could be caused by~~ mostly due to the lower Sun elevation in Warsaw during the near-noon measurements, and the larger ~~aerosol absorption. It appears that a slightly increased~~ optical depth of the city aerosols and increased cloudiness. It could be hypothesised that the expected stronger absorption of the solar UV radiation by urban aerosols ~~and properties of clouds generated over Warsaw are less important for the UV attenuation. In this work we are showing that the~~ is compensated here by a higher ~~city surface albedo compensates for the solar UV attenuation caused by urban aerosol load in the city of Warsaw~~surface reflectivity over the city.

1 Introduction

Excessive exposure to the ultraviolet radiation (UVR) reaching the Earth's surface has a detrimental impact on ~~the~~ human health. ~~Overexposure~~The overexposure to UV-B radiation (290-~~315nm~~315 nm) can cause erythema (redness of the skin), DNA and cellular damage (due to the generation of the reactive oxygen species), and ~~immunosupression~~immunosuppression. Longer UV wavelengths, UV-A (315-~~400nm~~400 nm), can be ~~cancerogenetic~~cancerogenic but also responsible for photoaging~~,~~ and various eye diseases, including ~~cataract. Both overexposure to~~cataracts. Overexposure to both UV-B and UV-A could lead to increased risks of cutaneous melanoma, non-melanoma skin cancers, and various health problems (e.g. Marionnet et al., 2014; Greinert et al., 2015). While UV-B is strongly ~~depended~~dependent on the latitude and thickness of the ozone layer, ~~UVA~~UV-A, especially UV-A1, the so-called long-wave UV-A (340-~~400nm~~400 nm), is ozone independent, more intense, and less variable with latitude (Sabziparvar et al., 1999).~~ The absorption by SO_2 (in the UV-B range) and NO_2 (mostly in the UV-A range) is important for the surface UV attenuation only in extreme concentrations of such gases. The surface intensity of UV depends significantly on properties of clouds and aerosols.The negative trends in these variables, found over many of the northern hemisphere midlatitudinal sites in the 1989s and 1990s, lead to increases of both the UV-B and UV-A irradiance (e.g. Krzyścin et al., 2011; Zerefos et al., 2012; De Bock et al., 2014).~~ In the spectral range up to ~330 nm, absorption by ozone is usually much stronger than absorption by other main trace gases (SO_2, NO_2) (Cede et all, 2006).

~~An~~The intensity of the solar UV radiation at the earth's surface depends significantly on properties and amount of clouding and aerosols. Upward UV-B and UV-A trends have been reported over several mid-latitudinal sites of the northern hemisphere since the beginning of the 1990s, which have been mainly attributed to decreasing attenuation by aerosols and clouds (e.g. Krzyścin et al., 2011; Zerefos et al., 2012; De Bock et al., 2014).

Attenuation of the incoming solar radiation seems to be higher over ~~the~~ large urban ~~agglomeration~~agglomerations relative to ~~the~~ surrounding rural areas due to the excessive light scattering and absorption by ~~the~~ anthropogenic aerosols. Papayannis et al. (1998) found differences between ~~UV~~ cloudless-sky UV irradiances measured over Athens and ~~its suburbs~~a suburban area near Athens. In Athens, the concentration of atmospheric aerosols was higher than at the ~~outskirts~~suburban site. The erythemal irradiance at the centre of Athens was up to 30% lower than at the ~~suburbs with similar values of total ozone (TO_3) for~~ suburban site during days with increased air pollution ~~in~~over the ~~air. Similar~~Athens basin. A similar difference was noticed ~~on the basis of the numerical simulations of~~in the modelled UV-B irradiance with input from measurements of the total ozone (TO_3) and aerosols optical depth (AOD) by the Brewer spectrophotometer (BS) at the outskirts of Athens. Acosta and Evans (2000) measured ~~the~~ erythemal irradiances in the centre and suburbs of Mexico City in the period 1994-1995. During ~~the~~this period in winter, the erythemal irradiance was 9% greater ~~at~~in the suburbs than in the centre of Mexico City, while during ~~the~~ summer, the recorded values were up to 43% greater (the mean value was 21%). Corr et al. (2009) found ~~for Mexico City aerosols enhanced~~strong absorption ~~at UV wavelengths with~~of UVR by urban aerosols over Mexico City with a single scattering albedo (SSA) in the range 0.7-0.85. Even larger attenuation (~ 60%) of the UVR due to ~~atmospheric~~ aerosols ~~of ~ 60%~~ was reported in Guangzhou, China, in the dry season from October ~~up~~ to January (Deng et al., 2012). Kazadzis et al. (2009a) found that ~~at~~for some cloudless days, differences in AOD among three sites (an urban, rural, and industrial area) located in Thessaloniki and at the outskirts of the city can ~~cause~~account for up to 20% differences in the UV irradiance. ~~Meleti et al. (2011) and~~ Fountoulakis et al. (2016) noticed that ~~the surface UVR measured in~~trends in the amount of absorbing urban aerosols over Thessaloniki ~~may be sensitive to another characteristic of the atmospheric aerosols, the single scattering albedo of aerosols, which may~~might counteract the ~~effects~~expected UVR increase due to the long-term decrease of AOD ~~changes~~ there.

The atmosphere over Poland is one of the most ~~dust~~particulate matter (PM) polluted in Europe. ~~The~~ PM10 and PM2.5 levels measured in Warsaw, as well as in most other larger cities in Poland, exceed the tolerable PM limit many times during ~~the~~a year (Polish Ministry of Environment, ~~2012~~2014). However, Zawadzka et al. (2013) analyzed ~~the~~ measurements taken by the Microtops II and CIMEL sunphotometer and stated~~,~~ that a small positive bias for AOD at 500 nm between Warsaw and a rural site (Belsk~~),~~) which is ~~in~~ ~60 km ~~distance from the city in the~~ south-west ~~direction,~~of the city was not larger than 0.02, whereas for ~~greater~~lower values of wind velocity ~~it~~the difference reached 0.04. The bias calculated from satellite measurements with ~~the~~ MODIS (Moderate Resolution Imaging Spectroradiometer) was ~0.05. The authors did not ~~claim~~find any significant differences in the Angström parameters between the sites for the visible ~~ranges~~range, so it could be ~~hypothesized,~~hypothesised that AOD values in the UV range also differ only slightly.

~~The geophysical variables possibly affecting the~~ However, for organic particles, the absorption in the UV range may be larger than predicted using Angström parameters for the visible range of the spectrum (Bais et al., 2015). Similar differences ~~in the ground level of the surface UVR~~ between ~~a city and remote sites are: clouds, aerosols, and surface albedo.~~ Warsaw and Belsk were reported by Chubarova et al. (2011), who analised results of aerosol measurements by the CIMEL sunphotometers located in Moscow (megacity with a population over 10 million) and Zvenigorod (population of approx. 16 thousand).

It seems possible that a large urban agglomeration could ~~produce~~generate specific cloud properties (due to the heat island effect and creation of ~~a~~ specific cloud condensation nuclei consisting of urban aerosols), higher loading of aerosols, and higher albedo~~.~~ than that in urban sites. The working hypothesis is that the Warsaw agglomeration produces a kind of shield against the incoming UV radiation. We will strive to support (or disprove) the hypothesis by comparing the erythemal and UV-~~A1~~A (324 nm) radiation measurements by the BSs in Warsaw and ~~at~~ Belsk for the period May 2013-December 2015.

2 Methodology

Monitoring of the UV spectra by BS is carried out by the Institute of Geophysics, Polish Academy of Sciences (IGF PAS), at the Central Geophysical Observatory Belsk since 1992 by the single monochromator BS~~ No.~~, serial number 64~~,~~ (BS064), and in Warsaw since 2013 by the double monochromator BS~~ No.~~, serial number 207 (BS207) installed on the roof (elevation ~25 m above street level) of the IGF PAS main building. Previously, ~~BS 207~~BS207 was working at Belsk (2010-2013). Comparison of ~~BS No. 64~~BS064 and ~~BS No. 207~~BS207 for that period will allow us to assess the differences between the measured UV doses due to ~~the~~ instrumental differences. ~~In the middle of 2013 BS 207~~BS207 was moved to Warsaw in the middle of 2013.

The present study focuses on differences in the erythemal and UV-~~A1 (340-400~~A (324 nm) doses measured by the BSs in Warsaw (52.3ºN, 21.0ºE, 130 m amsl) and ~~at~~ Belsk (51.8ºN, 20.8ºE, 190 m amsl~~), which~~). The wavelength 324 nm was chosen because it is one of the longest wavelengths measured directly by both BSs and the gaseous absorption by the main trace gases (O_3, NO_2, and SO_2) is weak at this wavelength. The Belsk observatory is located in a rural region (the largest orchard region in Poland) ~~at a distance of about 60 km in the south-west direction from the city (~~far from ~~the~~ urban and industrial developments~~). The Warsaw~~ . Surroundings of the city measuring site ~~is located in the area, which is a mixture of different surfaces:~~consist of grass , trees, concrete constructions (buildings, pedestrian footpaths), and asphalt roads.

BS064 is an older generation instrument - Mark II type, which is equipped with ~~the~~a single monochromator. Its spectral range is 290-325 nm in 0.5 nm steps and ~~the~~a spectral resolution of 0.6 nm (FWHM). The ~~spectra~~spectral accuracy decreases for ~~greater~~higher values of AOD and for larger solar zenith angles, i.e. for cases with an enlarged contribution of the diffuse component in the total UV radiation~~,~~ that increases the stray-light effect on the instrument. Furthermore, it does not have a ventilation system. The quality control of its performance has been assessed by almost yearly calibration against the travelling world standard BS~~ No.~~, serial number 17 ~~. BS No. 17~~(BS017). BS017 itself is regularly compared with ~~the~~a set of three Brewer instruments, so-called “Brewer reference triad” (Fioletov et al., 2005). ~~BS No. 64~~BS064 was also compared with Bentham DM-150 during the project Quality Assurance of Spectral Ultraviolet Measurements (QUASUME) in May ~~2014~~2004 (Gröbner et al., 2005, 2006). The estimated 1σ uncertainty of the erythemal irradiance is about 5~~%.~~% (Gröbner and Schreder, 2004).

BS207 is the newest type instrument - Mark III, ~~that~~which is equipped with a double monochromator reducing significantly the stray-light effect. It is also equipped with ~~the~~a ventilation system~~,~~ which prevents overheating of the instrument during hotter days. ~~The~~Its spectral characteristics are the same as BS064, however the spectral range is ~~290-363nm in 0.5 nm steps with almost similar~~wider extends to ~~BS064 spectral resolution~~363 nm. BS207 ~~is~~was calibrated against BS017 in 2012 and 2013. After the calibration in 2013, it was moved to Warsaw. Furthermore, it has been calibrated 3 to 4 times per year since 2010 with a set of standard lamps ~~yielding ~5%~~that allows elimination of ~~measurement spectrum error.~~instrument ageing (loss of its sensitivity to UVR). For both instruments, the SHICRivm software ~~has been~~was used to extend the spectra up to 400 nm and to eliminate erroneous spectra (Slaper et al., 1995).

The erythemal irradiance is calculated as the integral over the wavelength ~~of the~~range 290-400 nm BS spectra after the SHICRivm ~~standardization~~standardisation, which ~~are~~is weighted by the erythemal action spectrum. The ~~integration for~~ UV-~~A1~~A (324 nm) irradiance is taken without any weighting. The erythemal action spectrum ~~follows~~ is that suggested by the Commission Internationale de l'éclairage (CIE ~~(~~) (CIE, 1987). Further, the partly daily erythemal and UV-~~A1~~A (324 nm) doses are calculated as ~~the~~a time integral of the pertaining ~~irradiances~~irradiance for the 6h period for all~~-~~-sky~~-~~ conditions (local noon ~~±~~ -3h, local noon +3h) and the 3h period for cloudless-sky conditions (local noon-3.5h, local noon-0.5h). ~~Solar noon is computed from the astronomical formulas corresponding to the specific day of the year.~~ Cloudless-sky conditions are identified using ~~the following~~a two ~~steps~~step algorithm. ~~First~~The first step is ~~the approximate searching~~a preliminary search for such days using the ~~following~~ criterion: the solar UV irradiance derivative with solar zenith angle is negative. In the next step, the smoothness of the time series for the day~~,~~ which ~~meet~~fulfilled the first criterion, is examined, i.e. the bell-shape of the UV ~~spectrum~~time series must be ~~preserved. In case of jumps in the series such day is omitted.~~ identified. There is no strict mathematical criterion applied here, but rather an intuitive inspection of the time series shape.

Ratios between doses measured by BS064 and BS207, based on collocated observations at Belsk ~~in~~for the period October 2010 – April 2013, allow us to estimate the uncertainty range ~~for~~of the ratio related to differences in BS instrumental characteristics and in time of observations. The BS measurements are not ~~synchronized~~synchronised, as the spectrum ~~length is~~ranges are different. The same ratio is measured ~~in~~for the period of the Warsaw observations (May 2013 to December 2015) by BS207 to assess the impact of the urban agglomeration ~~impact~~ on the erythemal and UV-~~A1~~A radiation. The LOWESS (Locally Weighted Scatterplot Smoothing) filter (Cleveland, 1979) was used for smoothing of the curves.

~~Numerical simulations for the cloudless sky conditions of the ratio between the partly daily doses measured in Warsaw and at Belsk permit us to estimate the UV differences between the sites, caused by the geographical location, as Belsk is more to the south, TO$_3$, and the surface albedo (lower for surfaces covered by plants). The FastRT model for cloudless sky is used to calculate the spectral irradiance (Engelsen and Kylling, 2005) and erythemal doses. Following model input parameters are selected for such calculations: daily mean total ozone routinely measured by BS, fixed aerosols characteristics representing the mean values derived from the Belsk's CIMEL sunphotometer (AOD at 340 nm=0.32, single scattering albedo=0.92), fixed albedo of 0.03 for Belsk and a set of albedo values for Warsaw that is typical for the various urban surfaces.~~

Numerical simulations for the cloudless-sky conditions of the ratio between Warsaw and Belsk were performed to calculate differences caused by various factors, such as the geographical location (Belsk is slightly to the south), TO$_3$, surface albedo, and aerosols properties (AOD, SSA). Simulations were performed with the radiation transfer model (RTM) libRadtran (Mayer and Kylling, 2005). The following model input parameters, which are from the simultaneous measurements at both sites, are used in calculations: daily mean total ozone by the BSs standard measurements, AOD at 550 nm measured by the MODIS for the period 2013-2015. MODIS Aerosol Product values are available globally and include AOD at 550 nm over land and ocean. Remote sensing of aerosol properties using MODIS is presented by Ichoku et al. (2004). In this study, we used arrays of Level 2 (MOD 04, Collection 6) data produced daily at the spatial resolution of

10×10 km pixelation. From satellite data, we selected daily mean values of AOD from the nearest pixel to the measurement sites. Other input parameters are constants representing typical values used in the UV modelling, e.g. albedo of 0.03 for rural surfaces and SSA=0.92, which is a mean value measured by the CIMEL sunphotometer at Belsk (level 1.5 from AERONET – Aerosol Robotic Network) at 440 nm (http://aeronet.gsfc.nasa.gov). We used SSA at 440 nm as a constant for the whole ultraviolet spectrum, as it was found that monthly averages estimated from BS at Uccle were in close agreement with the CIMEL measurements at 440 nm, especially for 320 nm (Nikitidou et al., 2013). Furthermore, Liu et al. (1991) performed Mie calculations for the rural aerosol model (Shettle and Fenn, 1979) and suggested that for this type of aerosol, SSA is approximately independent of wavelength. There are no measurements performed for SSA at the UV wavelength range. To identify the impact of the selected parameter on the ratio between the sites' doses we use the RTM model, allowing variability only for this parameter and keeping constant other RTM input parameters. For example, to quantify the dependence of the ratio on the geographical location of the sites the RTM simulations were performed using fixed TO$_3$, AOD, and time (10:40 GMT), but the simulations were for consecutive days throughout the whole year.

3 Results

3.1 ~~Instruments comparison~~Comparison between measurements at Belsk

In the period from October 2010 to April 2013 both BSs were working simultaneously at Belsk. Figure 1a shows the time series of the measured ratio (BS064/BS207) between the 6h erythemal all-sky doses. The mean value of the ratio is 1.02 ± 0.07(1σ). Figure 1b illustrates that the 1-1 relation between the doses is appropriate for the whole range of ~~the~~ measured irradiances. The coefficient of determination based on this data set is 0.99. The mean ratio for UV-~~A1 range~~A (324 nm) is 1.~~01~~02 ± 0.07(1σ) for all-sky conditions.

~~The most of the differences lie within ±5% range but sometimes outliers~~Outliers greater than 10% sometimes appear, as the measurements were not synchronous. It is difficult to have ~~synchronized~~synchronised measurements by our BSs, as the scanning time is different~~,~~ because of the ~~length of the spectrum~~various spectral ranges, i.e. 290-325 nm for BS064 and 290-363 nm for BS207. ~~BS 064~~BS064 measures UV spectrum three times per hour, ~~while BS 207~~BS207 only two times per hour. Thus local cloudiness may be a source of large standard deviations of the mean ratios calculated during~~-~~ all~~-~~-sky conditions. To remove the effect of cloudiness, we ~~analyze~~analysed the ratios derived from 3h cloudless-sky measurements before solar noon. The cloudless-sky doses were calculated for ~~the~~a shorter period compared to those for the all-sky conditions, as cloudless-sky conditions in Poland usually prevail before noon.

Figure 2a shows the time series of the measured BS064/BS207 ratio for the cloudless-sky conditions and the corresponding scatter plot (Fig.2b). The mean value of the ratio is 1.01 ± 0.03 (1σ) and there is almost a 1-1 relation between the erythemal doses by both BSs. That is also supported by high value (0.998) of the coefficient of determination. For UV-~~A1~~A (324 nm) doses, the ratio is 1.00 ± 0.04 (1σ). Thus, the performance of BS064 and BS207 was practically the same during the Belsk's intercomparison. The agreement between the output of both BSs was almost perfect, suggesting that the instrumental differences did not have much influence on the ratio between the doses.

~~3.2 Numerical simulations~~

~~Part of the measured difference between both BSs, may be a result of the more northern location of the Warsaw site comparing to the Belsk site, different TO$_3$ over the sites, and surface albedo. In this sub-section, the modelled cloudless-sky doses over 6h period (+/- 3h to solar noon) are analyzed for Warsaw and Belsk. FastRT (Engelsen and Kylling, 2005) is used in the simulations taking into account real TO$_3$ values (i.e. daily mean TO$_3$ measured by BS using the so-called direct sun observations), fixed aerosol characteristics based on averaged results of CIMEL observations at Belsk, and prescribed values of surface albedo equal to 0.03 at Belsk and a set {0.03, 0.06, 0.12} in Warsaw.~~

~~Figure 3a shows the time series of the daily ratio of TO$_3$ measured at Belsk and in Warsaw. Figure 3b illustrates the scatter plot of the daily data. The mean ratio (BS064/BS207) from all data points presented in Fig.3a is 1.00 ± 0.01 (1σ). The correspondence between TO$_3$ values is found for the whole range of TO$_3$ variability at Belsk. All data points are in close proximity to the diagonal line representing the 1-1 relationship between the variables shown in the scatter plot. Thus, TO$_3$ is not a factor responsible for the UV difference between the sites. The erythemal doses calculated for the 6h near noon period with use of these ozone values, give the mean ratio 1.02 ± 0.02(1σ) for simulations assuming the surface albedo is equal to 0.03 (typical for rural regions) for both sites (see Fig.4 for the results with the mark "alb=0.03"). Thus, the TO$_3$ spatial variability and the geographical location of the site contribute only slightly to the UV differences between the sites.~~

~~Usually (in snowless periods) the urban albedo is higher than that in rural site and it provides somewhat higher intensity of the surface UV. Figure 4 presents simulations of the ratio between 6h near noon erythemal doses between the sites assuming the surface albedo is equal to 0.03 at Belsk but 0.06 or 0.12 in Warsaw. We have selected these values for the urban albedo in UV range based on Castro et al. (2001) experimental data over asphalt sites and grey surface-cement sites respectively, taken in Mexico City metropolitan area. The mean ratio derived from all the data points shown in Fig.4 is 1.00 ± 0.02 (1σ) and 0.98 ± 0.02 (1σ), for the Warsaw surface albedo equal to 0.06 and 0.12, respectively. The surrounding of the Warsaw measuring site is a mixture of areas with grass, asphalt, and grey-cement surface, so it could be assumed that surface albedo in the surrounding of the station is of 0.06. It means that a slightly higher albedo over the urban site compensates the latitudinal effect of the UVR differences between the sites.~~

~~3.3~~3.2 Comparison ~~of erythemal and UV-A1 doses measured~~between measurements at Belsk and ~~in~~ Warsaw

BSs were working simultaneously in Warsaw and ~~at~~ Belsk in the period from May 2013 to December 2015. The erythemal and UV-~~A1~~A (324 nm) doses calculated for these sites ~~in the~~for 6h periods ~~symmetrical around~~ (local noon ~~for 6h~~ - 3h, local noon + 3h) for all-~~sky~~skies, and 3h ~~before noon~~periods (local noon - 3h, local noon-0.5h) for cloudless ~~sky conditions, are~~skies, were analyzed to find the Belsk-Warsaw ratio between the measured doses (BS064/BS207). If the ratio obtained during the cloudless-sky conditions differs significantly from that ~~previously~~ obtained during the cloudless-sky conditions ~~for~~during the Belsk's BSs ~~operating in Belsk~~intercomparison, it will allow us to estimate the effect of urban aerosols ~~effect~~ on the surface UVR. ~~The~~A similar approach with the use of all-sky data will also provide an estimate of the effect of urban cloud ~~effect~~ on the surface UVR.

Figure ~~5~~3 shows the time series of BS064/BS207 measured ratio for ~~the~~ erythemal doses (Fig. ~~5a~~3a) and the UV-~~A1~~A (324 nm) doses (Fig. ~~5b) doses~~3b) for cloudless-sky conditions simultaneously appearing both in Warsaw and ~~at~~ Belsk during 3h ~~before local noon~~measurements. The ratio oscillates around 1.05 within the range ~~\~~~between 0.9~~-~~ and 1.~~1~~2. The main reason for this scatter is using the interpolated erythemal (or UV-~~A1~~A) irradiance ~~value~~values at the beginning (~~3.5 h before~~ local noon-3.5h) and at the end (local noon-0.5h) of the calculated period. BS observations ~~were~~ rarely ~~made exactly at the starting and ending~~ coincided with these moments. Thus linear interpolated values were used, taken from observations closest to the beginning or to the end of the period, i.e. the irradiance values just outside the observing period were also taken into account. The mean value of the Belsk-Warsaw ratio is 1.06 ± 0.04 (1σ) and 1.~~03~~04 ± 0.04 (1σ) for the erythemal and UV-~~A1~~A (324 nm) dose, respectively. The ~~same~~corresponding values calculated for ~~all~~ 6h ~~near noon~~ doses ~~(Fig.6)~~ during all-sky conditions (Fig.4) are 1.08 ± 0.19 (1σ) and 1.~~05~~06 ± 0.~~17~~18(1σ), respectively. Much larger uncertainty ranges of the estimates for all-sky conditions are due to the cloudiness effects, but the mean values of the ratio are only slightly larger than those found during the ~~Belsk's~~Belsk intercomparison of the instruments. In spite of possible different cloud properties over Belsk and Warsaw during 6h measurements, the determination coefficient values are still high, i.e. equal to 0.96 ~~and 0.95~~ for ~~the~~ erythemal and UV-~~A1~~A (324 nm) doses. The 1-1 correspondence between doses is ~~kept~~maintained for the whole range of the data (Fig.~~7~~5).

~~Standard~~The standard statistical test for ~~the~~a difference in the mean values taken from two large samples of an unknown distribution (Daniel and Cross, 2013) ~~is~~was used to ~~evaluate,~~find out if ~~a higher~~the BS064/BS207 mean ratio obtained during Belsk-Warsaw comparison of BSs ~~relative to~~is significantly larger than the ~~mean~~ ratio found during the Belsk intercomparison ~~is statistically significant~~. The ~~working~~ hypothesis~~,~~ that the mean ~~values~~value of BS064/BS207 ratio ~~(both for cloudless-sky and all-sky conditions) are~~ is higher during the Belsk-Warsaw comparison~~,~~ is supported by the test at the significance level ~~>~~better than 0.01~~. We conclude that the urban agglomeration only slightly attenuate~~ both for cloudless-sky and all-sky conditions.

3.3 Sources of the Belsk-Warsaw differences in the erythemal and UV-~~A1 radiation. The aerosol effects are responsible for about 6% (or 3%) larger 3h erythemal (or UV-A1)~~A doses

The more northern location of the Warsaw site results in lower SZA of ~0.5° at ~~Belsk and cloud effects only slightly enlarge the Belsk-Warsaw~~ the same time for BSs observations. Other factors affecting the ratio between the measured doses at the rural and urban site during cloudless conditions are differences in TO$_3$, surface albedo, and aerosol properties (AOD or SSA). In this sub-section, the modelled cloudless-sky irradiances are analysed for Warsaw and Belsk to discuss sources of the BS064/BS207 ratio variability.

The difference~~,~~ in the geographical coordinates for the sites, which are based on the simulations of the erythemal and UV-A irradiances at 10:40 GMT (i.e. ~~~2% both~~ near local noon) throughout 2015 leads to slightly higher values at Belsk. The modelled ratio changes with SZA (Fig. 6). The average ratio over the whole year is 1.03 ± 0.02 (1σ) for the erythemal ~~and~~ irradiance and 1.02 ± 0.01 (1σ) for UV-~~A1 doses~~A (324 nm). For the warm period (from 15 May to 14 September) modelled ratios were 1.01 ± 0.003 (1σ) and 1.01 ± 0.002 (1σ), but for the cold period (from 15 September to 14 May) modelled ratios were 1.04 ± 0.01 (1σ) and 1.03 ± 0.01 (1σ) – for erythemal and UV-A (324 nm) irradiances, respectively.

The total ozone difference between the sites is quite small (Fig.7). The mean TO$_3$ ratio (BS064/BS207) taken from all coinciding daily TO$_3$ values is 1.00 ± 0.01 (1σ). All data points are in close proximity to the diagonal line representing the 1-1 relationship between the variables (Fig. 7b). The mean modelled ratios between the erythemal and UV-A (324 nm) irradiances calculated for the selected fixed SZA and the site measured TO$_3$ values are 1.00 ± 0.01 (1σ) and 1.00 ± 0.002 (1σ), respectively, for all considered SZAs (30º, 40º, 50 º and 60º). Thus, TO$_3$ is not a factor responsible for the UV difference between the sites.

The AOD effect on the Brewers' ratio is inferred from the RTM simulations based on the measured AOD at 550 nm by MODIS for the period 2013-2015 on days when the data were available for both sites. Daily AOD means are taken into consideration. The calculation was performed separately for various SZAs (40º, 60 º and 70º) and fixed SSA=0.92. Fig.8 shows that AOD at 550 nm is slightly higher over the city. The mean AOD is equal to 0.26 and 0.20 over the urban and rural site, respectively. RTM simulations performed using the observed AOD values for various fixed SZAs (40º, 60 º and 70º) yield the BS064/BS207 ratio is almost the same 1.02 ± 0.02 (1σ) for all considered SZAs, for the erythemal and UV-A (324 nm) irradiances.

4 Discussion and conclusions

Warsaw agglomeration has over 3.5 million population, with high pollution due to ~~the~~ heavy vehicle ~~emission~~emissions and industry (mainly electric ~~powers~~power), causing numerous cases over the EU air quality threshold~~.~~ (Monitoring System of Air Quality in Mazowieckie Region, http://sojp.wios.warszawa.pl/). Like other large cities, it is expected that Warsaw produces the well~~-~~-known heat island that makes specific boundary layer, i.e. in the boundary layer factors like wind, temperature, moisture, turbulence and energy budget fields differ from nearby rural sites (e.g. Fortuniak et al., 2005, Miao et al., 2009, Haberlie et al., 2015), allowing anthropogenic aerosols to reach higher atmospheric layers that may enhance AOD and affect cloud properties (e.g. level of cloudiness, droplet size, liquid water content). ~~Previous study of the Belsk-Warsaw differences in the aerosols properties (Zawadzka et al., 2010) revealed similar values of the Angström exponent and higher Warsaw AOD values at 500 nm of about 0.02 i.e., ~10% of the overall mean AOD at Belsk for this wavelength. Similar values were reported by Chubarova et al. (2011) analyzing the results of aerosols measurements by CIMEL sunphotometers located in Moscow (megacity with population over 10 million) and Zvenigorod.~~

The Warsaw agglomeration attenuates only slightly the erythemal and UV-A (324nm) radiation. Under cloudless conditions, the Belsk/Warsaw ratio between the erythemal and UV-A (324 nm) doses is ~1.06 and ~1.04, whereas the ratio is ~1.08 and ~1.06 for all-sky conditions, respectively. The aerosol effects are responsible for ~2% larger erythemal and UV-A near-noon doses at Belsk. The cloud effects add 2%, enlarging the Belsk-Warsaw difference. The SZA effects due to the longitudinal/latitudinal difference between the sites lead to 3% (or 2%) greater erythemal (or UV-A) doses at Belsk. The difference is even larger in the cold period of the year (for higher SZAs). The unexplained 1% higher doses at the rural site for the erythemal doses ratio could be attributable to instrument issues.

It seems possible that urban aerosols lead to higher absorption of the UV irradiance, i.e. small SSA values (<0.9) could characterise such aerosols. On the other hand, the albedo of urban surfaces is higher in the snowless period, that may compensate the effects of lower urban aerosols' SSA. Analysing the UV radiation in the Mexico City metropolitan area, Castro et al. (2001) found the urban albedo of 0.12 over asphalt and grey surface cement sites. This is four times larger than the commonly used albedo of 0.03 over grass. Parisi et al. (2004) found that over some non-shaded parts of the city with high albedo (e.g. concrete surface) there is an amplification of the human exposure of up to 7% for people in the upright position. ~~Using the value of the erythemal radiation amplification factor due to aerosols of 0.15, which is defined for AOD at 550 nm (Krzyścin and Puchalski, 1998), it could be estimated that 10% AOD difference between Belsk and Warsaw would induce ~2% attenuation of the erythemal doses in Warsaw. The present study, which is based on the measured UV spectra by BSs, shows higher difference (~6%) of the erythemal irradiance under cloudless-sky conditions due to the urban pollution effect. It seems possible that higher absorption of UV irradiance, i.e. smaller SSA by the anthropogenic aerosols, is a factor that may be responsible for larger attenuation of the surface UVR in Warsaw.~~

~~Fountoulakis et al.~~We performed RTM simulations with the observed TO_3 and AOD values over Warsaw to fully compensate (by absorbing aerosols) the UV increase due to changes in albedo from 0.03 to 0.12. SSA=0.86 and 0.85, for SZA=60° and 30°, respectively, are found for the city site, i.e., 0.06 and 0.07 less than the value previously used in our RTM simulations for rural aerosols. Such estimate looks probable, as the Warsaw observing site is among the most polluted parts of the city because of abnormal vehicle emissions in the nearby main city roads.

Fountoulakis et al. (2016) discussed factors important for the UV ~~spectra~~spectral variability in Thessaloniki. They pointed out that the cloudless-sky UV-A irradiances could be sensitive not only to AOD changes but also to SSA changes. Kazadzis et al. ~~Chubarova et al. (2011) analyzing~~(2009b) found that UV-A irradiance increase in Thessaloniki for the period 1998- 2006 cannot be explained only by the AOD changes, but also by the changes of SSA over the area, due to the improvement of the air quality there. Chubarova et al. (2011) analysing results by CIMEL sun photometers located in Moscow and in Zvenigorod (less polluted site) found that the uncertainty range of SSA is too high, precluding discussion of the SSA urban effects. However, they found that SSA in Moscow for the visible range of solar radiation was 0.02-0.03 smaller than that obtained ~~over~~from the clean site. It is worth mentioning that there is a lack of the direct retrieval to obtain SSA from UV spectral measurements. ~~Indirect~~An indirect method for BS ~~has been~~was proposed ~~(~~by Bais et al~~.,~~. (2005) depending on the assumed values of the asymmetry parameter, surface albedo, aerosol vertical profile, and the extraterrestrial solar spectrum.~~ They found that frequently low SSA values < 0.7 were observed in Thessaloniki when AOD at 340 nm was less than 0.3. It could induce 10%-20% attenuation of the irradiance at 340 nm relative to the case of SSA=0.92 being typical for clean sites. Based on their results we could estimate that ~5% decline of UV irradiance, which is attributed to the more absorbing Warsaw aerosols, is caused by aerosols with SSA ~0.8 at 340 nm. Such estimate looks probable as the Warsaw observing site is among the most polluted parts of the city because of the abnormal vehicle emission in the nearby main city roads.~~ ~~Kazadzis et al. (2009b) found that UV-A irradiance increase in the Thessaloniki for the period 1998- 2006 cannot be explained only by the AOD changes, but also by the changes of SSA over the area, due to improvement of the air quality there.~~

~~For all-sky conditions the attenuation of the surface UV radiation in Warsaw is only slightly higher than that found during cloudless-sky conditions, i.e. ~8% for erythemal doses and 5% for UV-A1 doses, which is ~2% greater than found for the cloudless-sky case. Cloud~~ The cloud effects should be more pronounced during the warm period of the year, where the city heat island may generate stronger convection than that ~~existing~~ in the cold period of the year. Romanov (1999) ~~analyzing~~analysing NOAA satellite images retrieved higher cloud cover in summer over~~ the~~ central Moscow compared to its suburbs. Inoue and Kimura (2004) found that in Tokyo there were more low~~–~~-level clouds in the summer period (July-August) ~~comparing~~compared to rural sites in Kanto region. Moreover, urban heat islands lead to more thunderstorm initiation episodes (e.g. ~~Sheperd~~Shepherd, 2005; Haberlie et al., 2015).

The classical theory (Twomey, 1977) states that when there are more aerosols high above the surface due to stronger updraft generated by the city warm island, aerosols serve as cloud condensation nuclei, reduce the size of cloud effective radius and increase the number of droplets, causing larger cloud optical thickness (COT) and finally higher attenuation of radiation reaching the Earth's surface. Thus, additional cloudiness generated over large cities may act as an umbrella against excessive UV radiation. We calculate BS064/BS207 ratio during Belsk-Warsaw comparison campaign taking into account measurements in the warm period, 15 May – ~~15~~14 September. We ~~expect~~expected to find a higher ratio for that period according to the classical theory stated above. However, the ratio is only slightly lower, i.e. 1.06 ± 0.17(1σ), for the erythemal doses, and 1.~~05~~06 ± 0.16(1σ) for UV-~~A1~~A (324 nm) doses~~. It~~, and part of this difference is the effect of different SZAs between the sites. This may suggest that contrary to ~~the~~ expectation, COT is smaller over ~~the~~ urban ~~area~~areas. Jin et al. (2005) discussed aerosol-cloud relationship over New York and ~~Huston~~Houston. They found that thick urban aerosols correspond to low COT there. Thus, it seems possible that ~~even higher~~increased cloudiness over urban areas does not necessarily mean ~~higher~~increased attenuation of solar radiation, ~~because the urban aerosols modify~~since modification of the cloud structure ~~compensating~~and properties by the urban aerosols may lead to the ~~effect of increased cloud cover there~~formation of clouds which attenuate the solar radiation less effectively.

~~A slightly higher BSO064/BS207 ratio is found during the cold period because of an effect of seasonal albedo changes, i.e. value 1.09 ± 0.20(1σ) was obtain using the winter data comparing to 1.08 ± 0.19 (1σ) found in the all year data. During winter, snow cover melts faster in the centre of Warsaw, due to the city warm island. Furthermore, snow is~~

~~systematically removed from the roads and pavements in the city. Snow during the Warsaw-Belsk comparison campaign was hardly observed thus the ratio was affected only slightly by the seasonal albedo differences.~~

~~Zerefos et al. (2012) discussed that present UV level over many sites in the northern mid-latitudes is high due to the positive trends in the UVR related to the decreasing total ozone (up to mid 1990s) and negative trends in amount of clouds and aerosols (up to mid 2000s). Figure 8 shows the annual erythemal means for the period 1976-2015 based on the updated (for the period 2009-2015) time series of the broad band UV measurements at Belsk (Krzyścin et al., 2011). The UV increase in Poland for the period 1976-2015 is especially strong as the cloudiness and amount of aerosols in the atmosphere in the mid 1970 and early 1980s was large, because of the enormous environment pollution during the communist era. The UV level stabilizes around 2006 and the present level of the erythemal irradiance at Belsk is ~15% larger than that in the mid 1970s.~~

Our study proves that the UV level in Warsaw is ~~only~~ slightly lower ~~(~5%-8%)~~ than that found in cleaner ~~surroundings of Warsaw. It seems that higher absorption of UV radiation by~~ suburbs of the city. Thus urban aerosols ~~(lower SSA values) is the main source of the urban UVR attenuation there. However, Parisi et al. (2004) found that over some non shaded part of the city with high albedo (e.g. concrete surface) there is an amplification of the human exposure of up to 7% for people in the upright position. Thus contaminated urban atmosphere~~and clouds over Warsaw ~~cannot be treated as a~~do not provide an effective shield against excessive ~~human exposure~~UVR.

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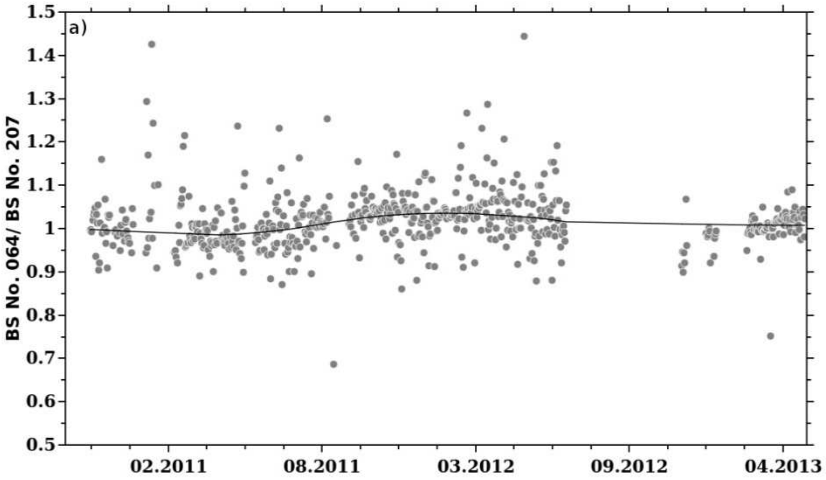
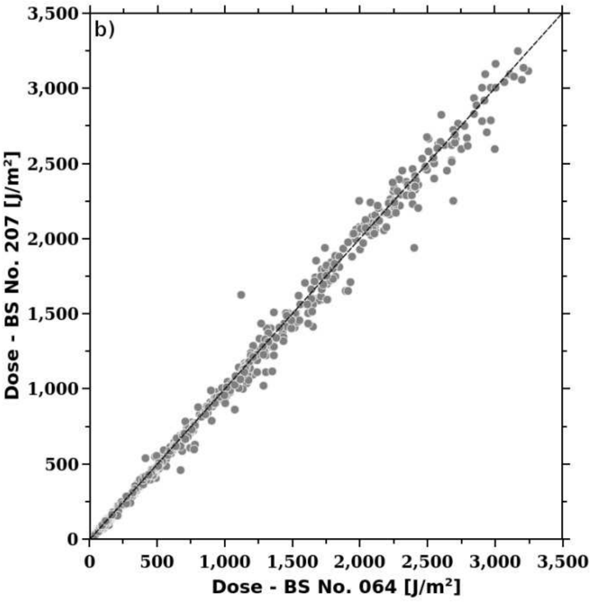
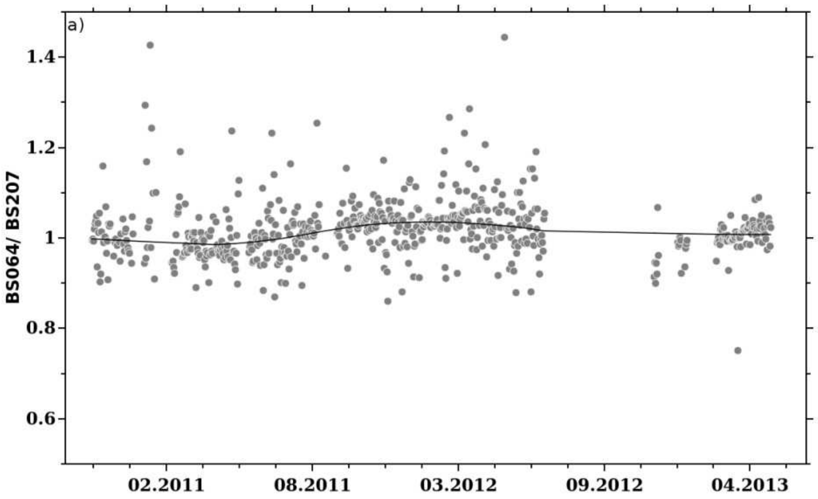

a)
BS No. 064/ BS No. 207
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
02.2011
08.2011
03.2012
09.2012
04.2013


b)
Dose - BS No. 207 [J/m²]
Dose - BS No. 064 [J/m²]
3,500
3,000
2,500
2,000
1,500
1,000
500
0
0
500
1,000
1,500
2,000
2,500
3,000
3,500



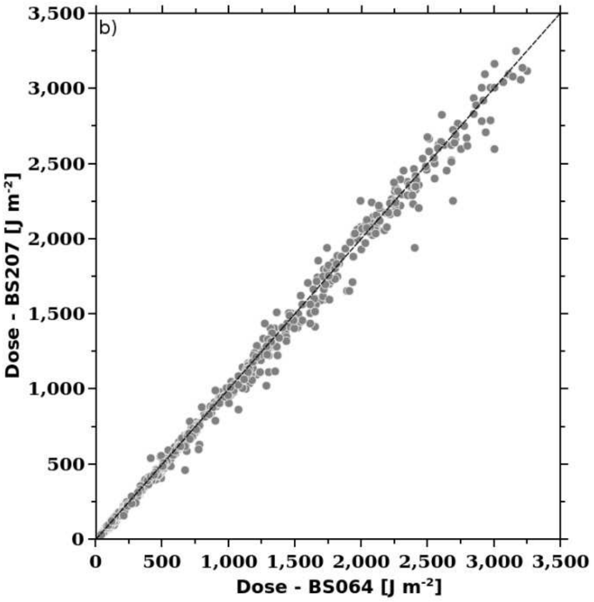
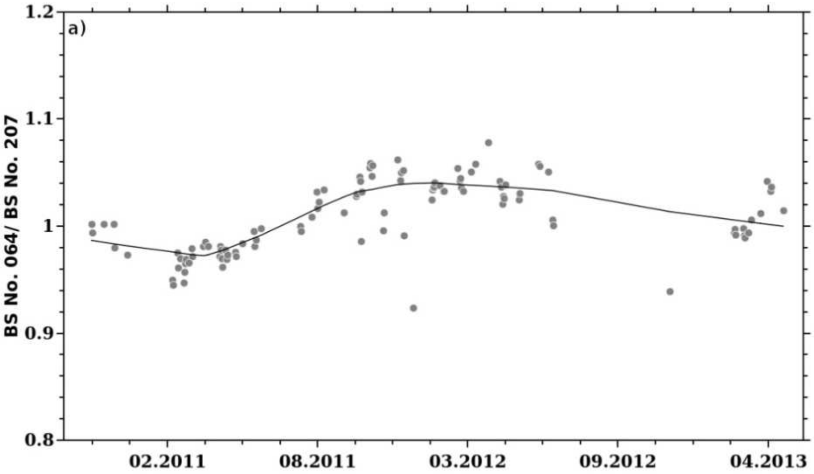
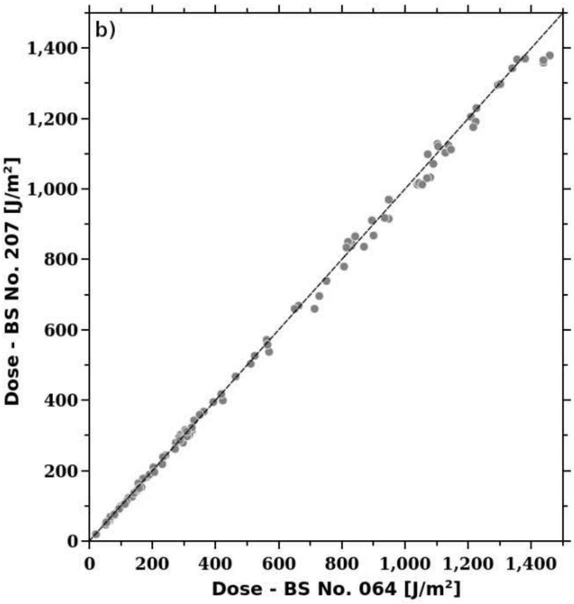
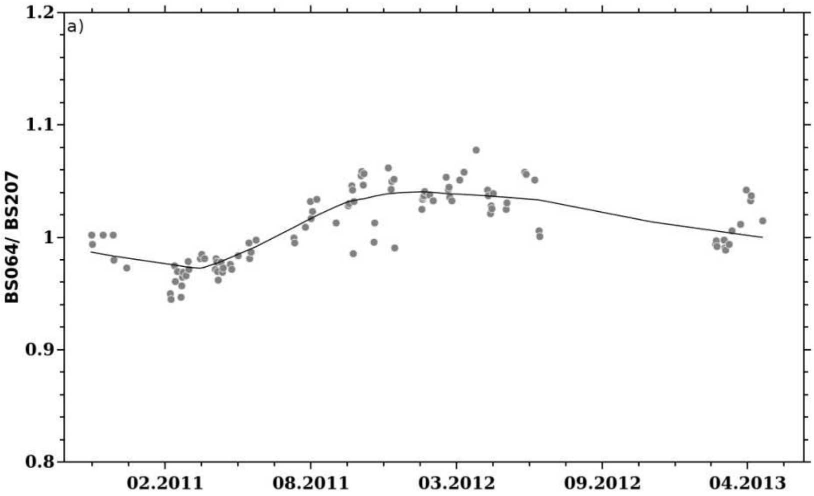


Figure 1a: The ratio between erythemal 6h (noon+/-3 hr) doses measured by the Brewer Spectrophotometer No. 64 and No. 207 while working simultaneously at Belsk (all-sky conditions). The solid curve ~~represent~~represents the smoothed data by LOWESS filter.

Figure 1b: ~~The~~Scatter plot of doses measured by ~~the~~ Brewer ~~spectrophotometer~~spectrophotometers No. 207 ~~versus those measured by the Brewer spectrophotometer~~and No .64.


a)
1.2
1.1
1
0.9
0.8
BS No. 064/ BS No. 207
02.2011
08.2011
03.2012
09.2012
04.2013


b)
1,400
1,200
1,000
800
600
400
200
0
Dose - BS No. 207 [J/m²]
0
200
400
600
800
1,000
1,200
1,400
Dose - BS No. 064 [J/m²]



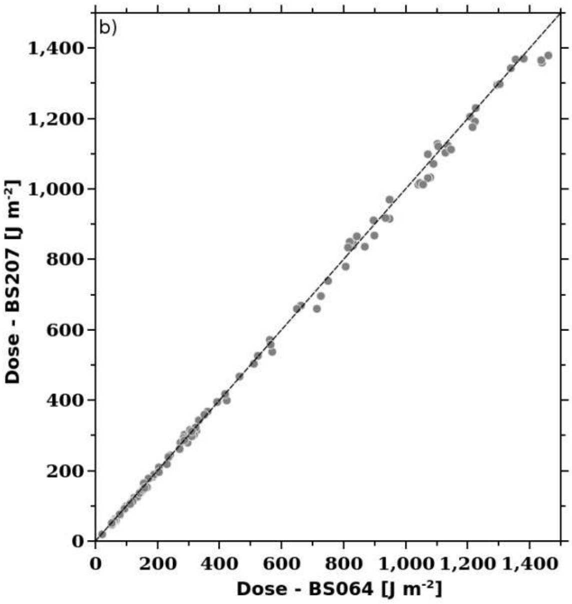
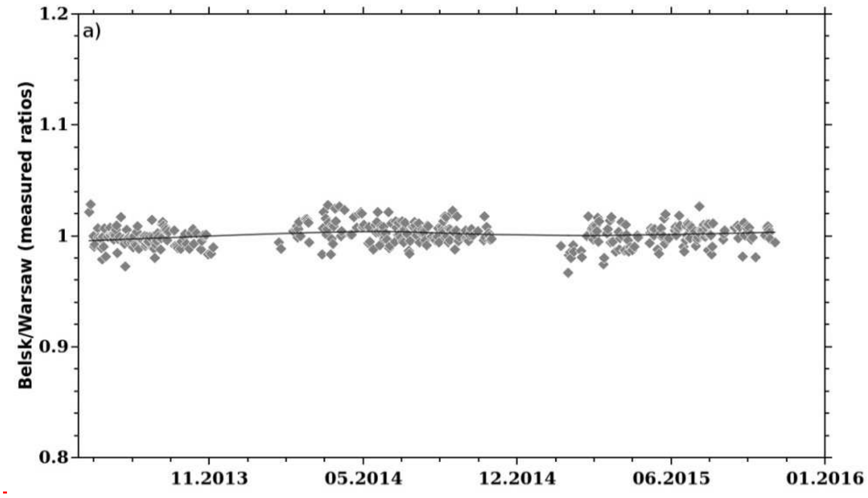
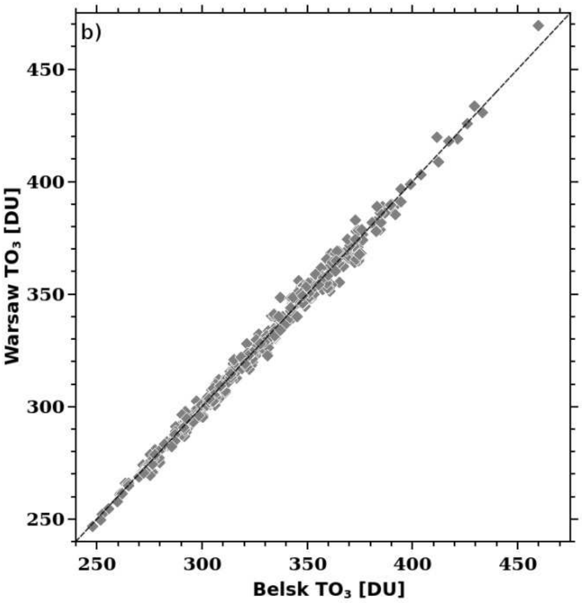


Figure 2a: ~~The same~~Same as Fig.1a but for cloudless-sky conditions and 3h doses calculated for the period before noon (noon-3.5h, noon-0.5h).

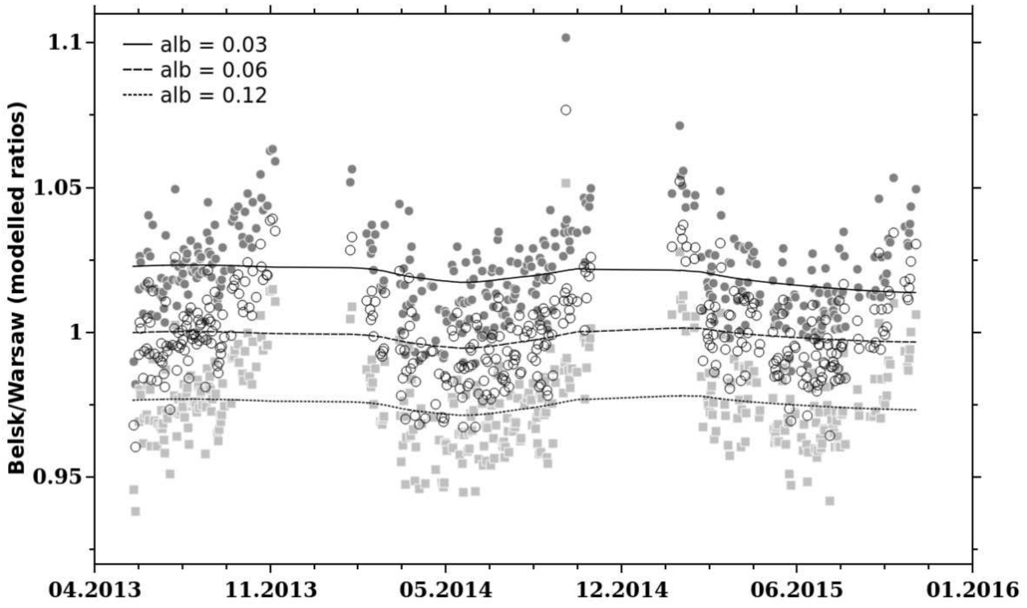
Figure 2b: ~~The same~~Same as Fig.1b but for cloudless-sky conditions and 3h doses calculated for the period before noon (noon-3.5h, noon-0.5h).

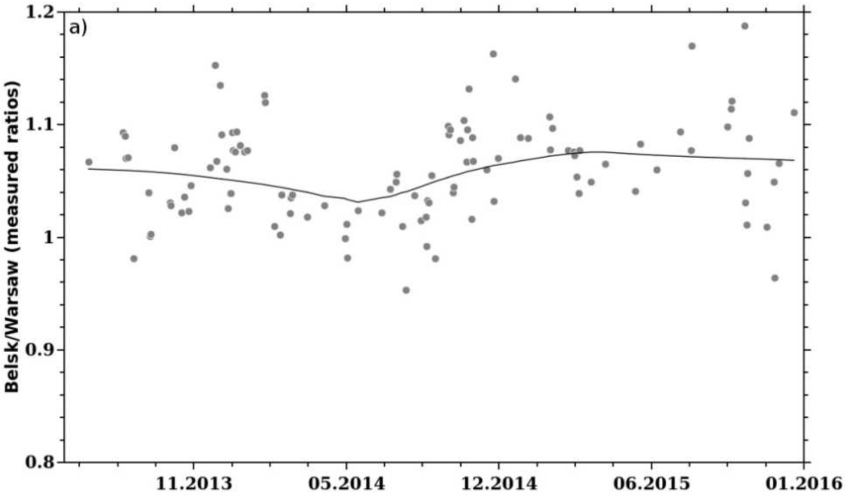




~~**Figure 3a: The ratio between total ozone values measured by the Brewer Spectrophotometer No.64 and No.207 while working simultaneously at Belsk and in Warsaw for the period May 2013-December 2015. The solid curve represent the smoothed data by LOWESS filter.**~~

~~**Figure 3b: Total ozone values measured by the Brewer Spectrophotometer No.64 versus total ozone values measured by the Brewer spectrophotometer No.207 while working simultaneously at Belsk and in Warsaw for the period May 2013-December 2015.**~~


alb = 0.03
alb = 0.06
alb = 0.12
Belsk/Warsaw (modelled ratios)
1.1
1.05
1
0.95
04.2013
11.2013
05.2014
12.2014
06.2015
01.2016


a)
Belsk/Warsaw (measured ratios)
1.2
1.1
1
0.9
0.8
11.2013
05.2014
12.2014
06.2015
01.2016

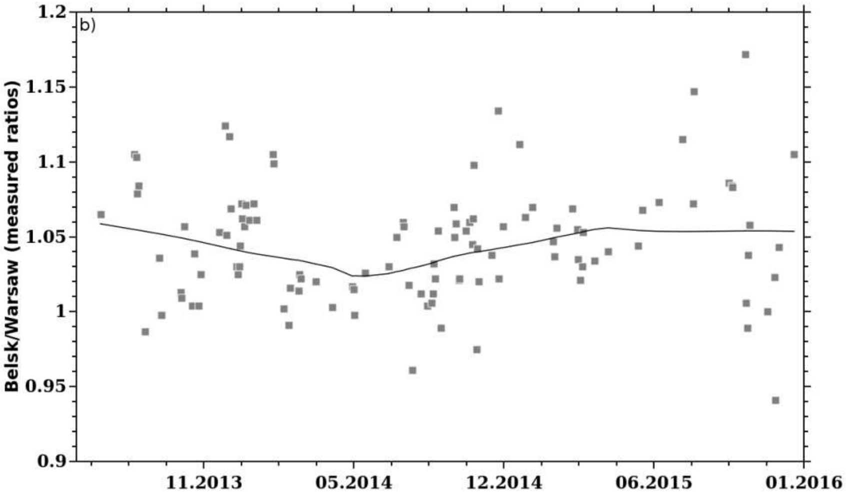
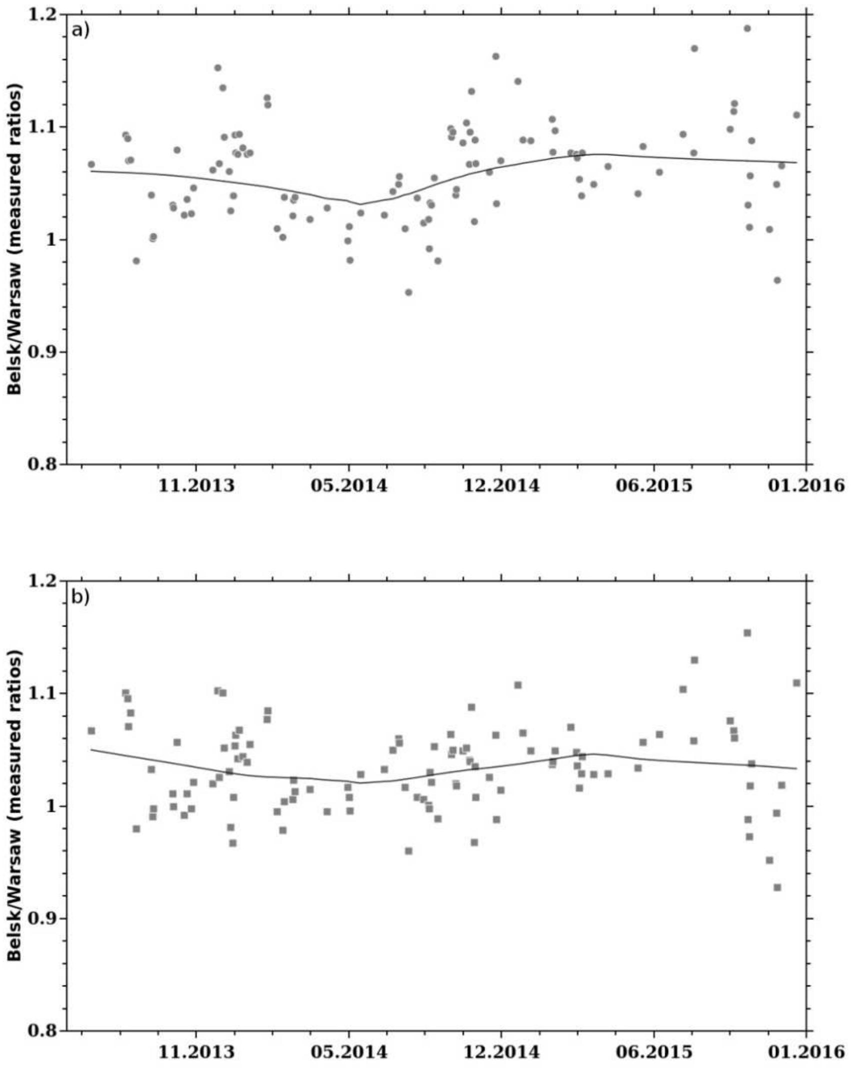
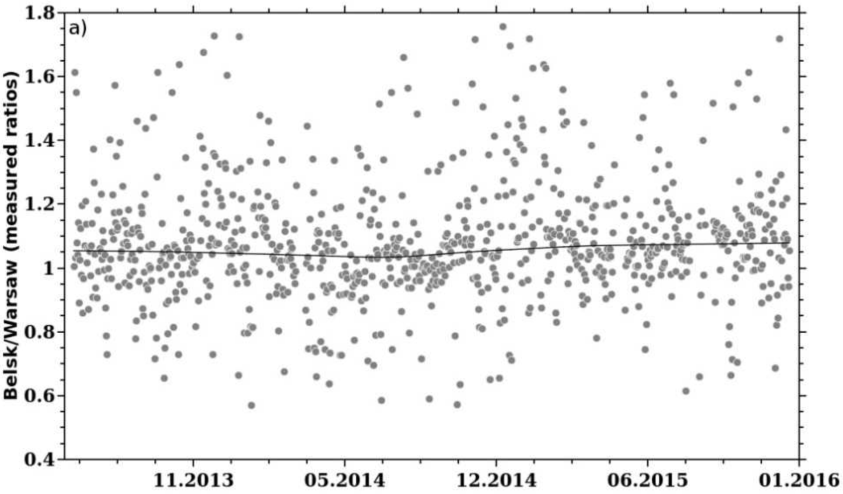
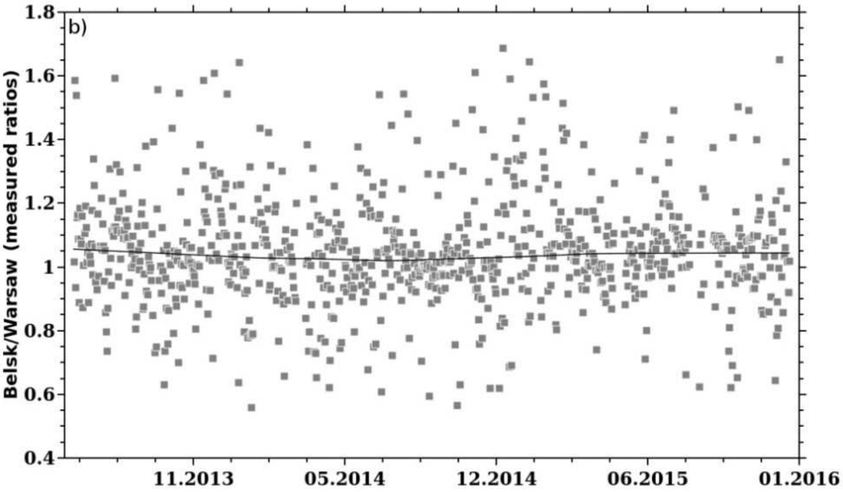


Figure 3~~4: The Belsk/Warsaw ratio between partially daily 6 hr doses (local noon +/- 3h) calculated by FastRT model with following input values: total column amount of ozone measured by the Brewer spectrophotometer, SSA=0.92, AOD=0.32 at 340 nm, surface albedo 0.03 at Belsk and {0.03, 0.06, 0.12} in Warsaw. The solid curve represent the smoothed data by LOWESS filter.~~



~~Figure 5: The Belsk/Warsaw ratio between the partially~~: The Belsk/Warsaw ratio between the partial daily 3h doses (noon-3.5h, noon-0.5h) measured during cloudless-sky conditions existing over both sites for erythemal doses (a) and UV-~~A1~~A (324nm) doses (b). Solid curves represent the smoothed data by LOWESS filter.


a)
Belsk/Warsaw (measured ratios)
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
11.2013
05.2014
12.2014
06.2015
01.2016


b)
Belsk/Warsaw (measured ratios)
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
11.2013
05.2014
12.2014
06.2015
01.2016

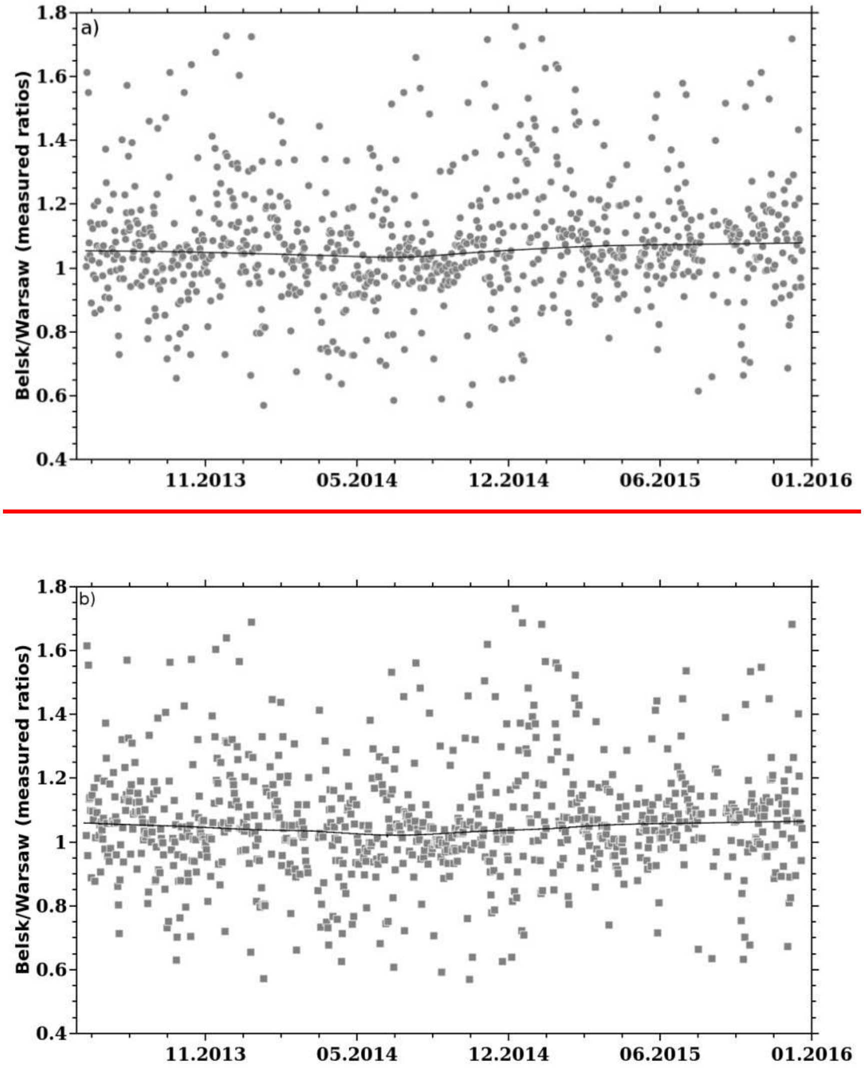
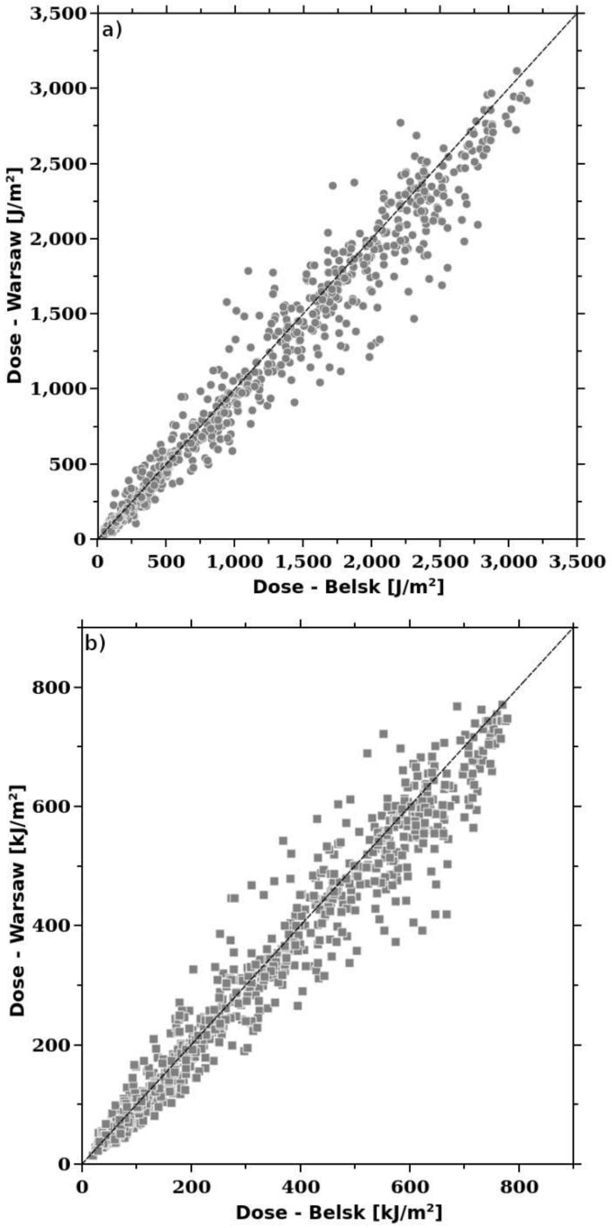


Figure 4~~6~~: ~~The same~~Same as Fig.5 but for the near noon ~~partially~~partial daily dose (noon-3h, noon+3h) for all-sky conditions. Solid curves represent the smoothed data by LOWESS filter.

~~**Solid curves represent the smoothed data by LOWESS filter.**~~


a)
Dose - Warsaw [J/m²]
Dose - Belsk [J/m²]
0
500
1,000
1,500
2,000
2,500
3,000
3,500
b)
Dose - Warsaw [kJ/m²]
Dose - Belsk [kJ/m²]
0
200
400
600
800

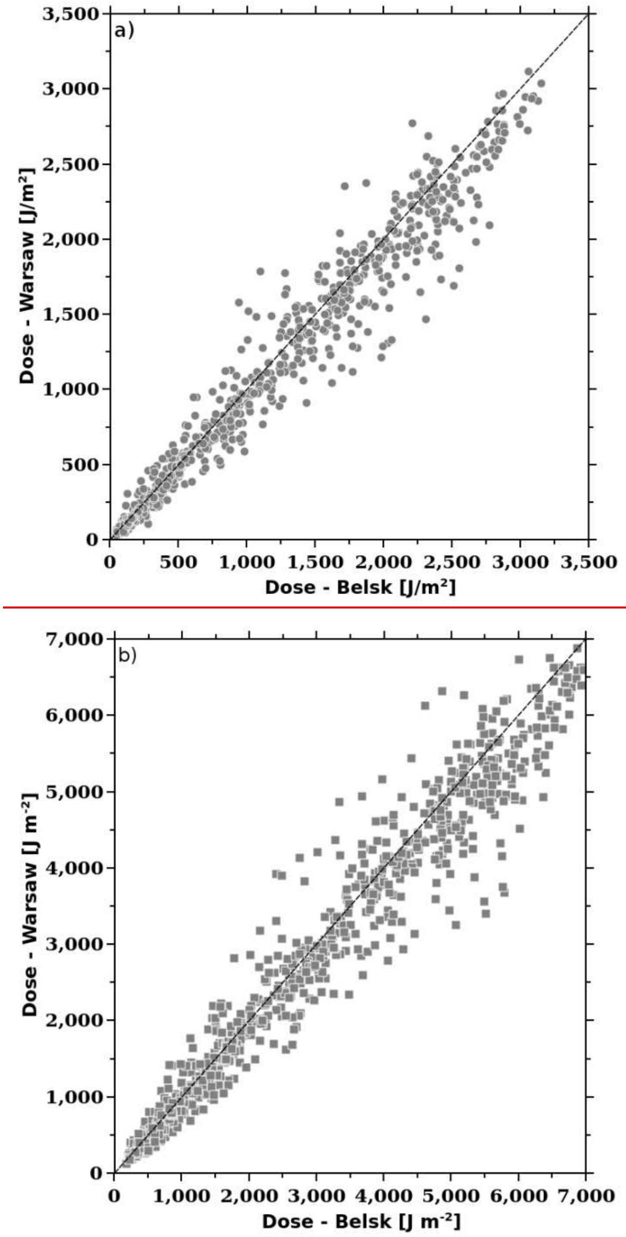
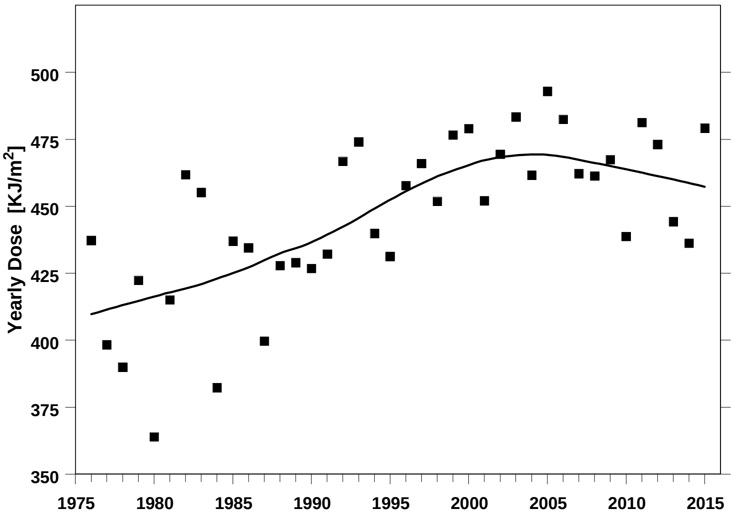


Figure 5~~7: Partially~~: Scatter plot of partial daily ~~near noon~~ doses ~~[~~(local noon-3h, local noon+3h~~]~~) measured in Warsaw ~~versus those at~~and Belsk: erythemal doses (a) and UV-~~A1~~A (324nm) doses (b).


Yearly Dose [KJ/m^2]
350
375
400
425
450
475
500
1975
1980
1985
1990
1995
2000
2005
2010
2015

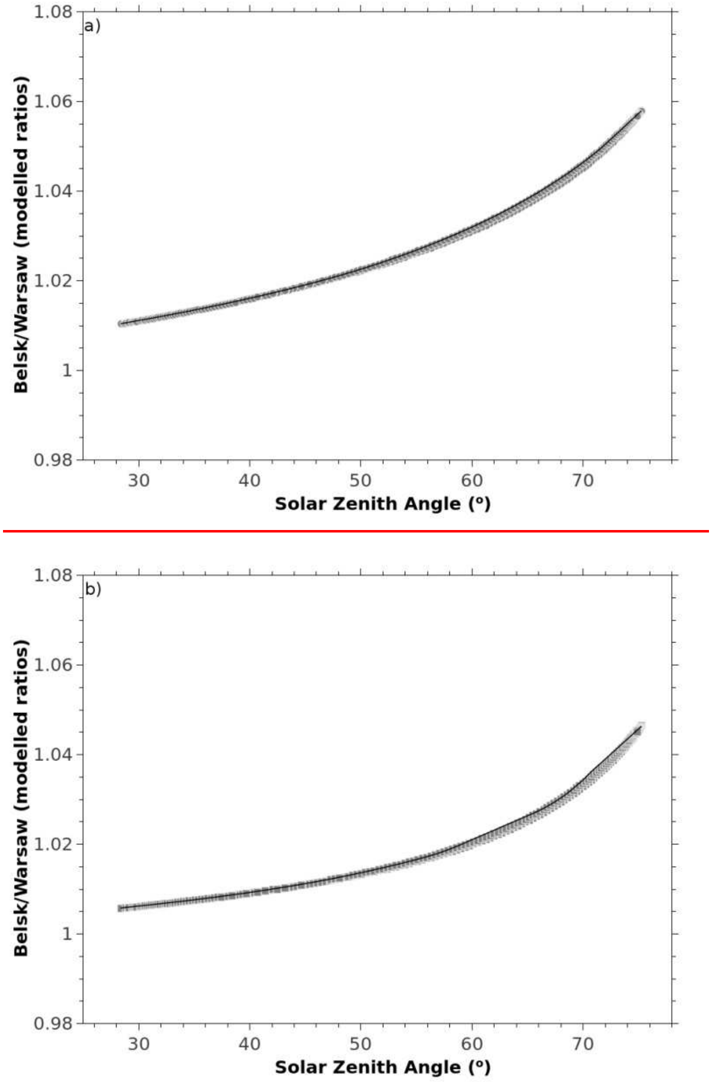
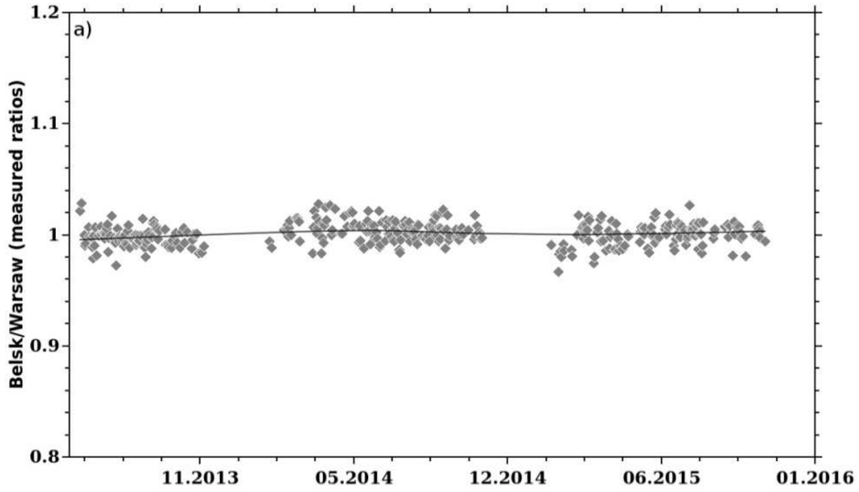


Figure 6~~8: Yearly means of the~~: The Belsk/Warsaw ratio between erythemal ~~dose measured~~ (a) and UV-A (324nm) (b) irradiances calculated by the libRadtran model for 2015 versus SZA at Belsk for the ~~period 1976-2015 at Belsk (squares~~10:40 (GMT). The solid curve ~~denote~~represents the smoothed data by LOWESS filter.



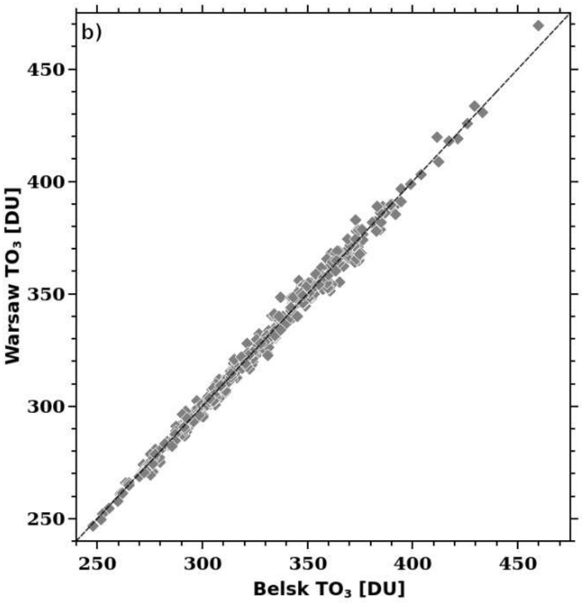
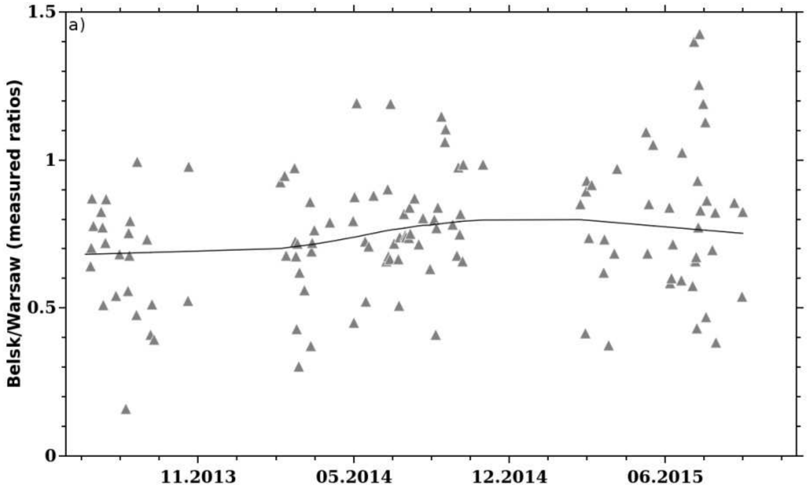


Figure 7a: The ratio between total ozone values measured by the Brewer Spectrophotometer No. 64 and No. 207 while working simultaneously at Belsk and in Warsaw for the period May 2013-December 2015. The solid curve represents the smoothed data by LOWESS filter.

Figure 7b: Scatter plot of total ozone values measured by the Brewer Spectrophotometers No. 207 and No. 064 while working simultaneously at Belsk and in Warsaw from May 2013 to December 2015.



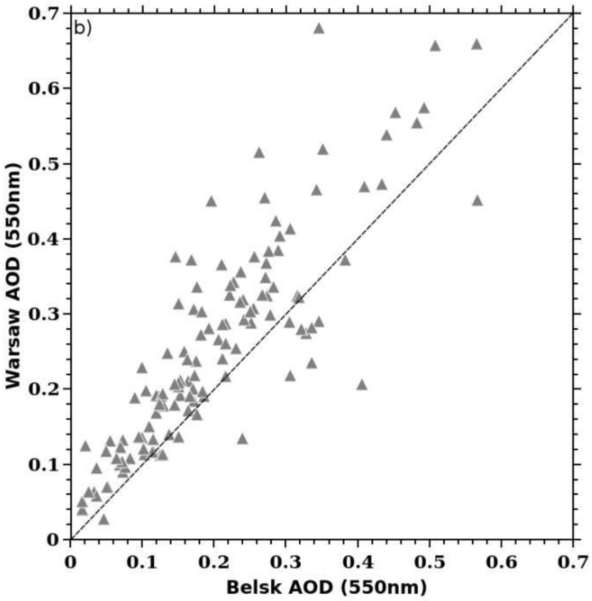


Figure 8a: The ratio between AOD at 550nm measured simultaneously by MODIS over Belsk and Warsaw in the period May 2013-December 2015. The solid curve represents the smoothed data by LOWESS filter.

Figure 8b: Scatter plot of AOD at 550nm measured by MODIS over Belsk and Warsaw from May 2013 to December 2015.