Measurements of Aerosols and Trace Gases in Southern Romania

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An intensive measurement campaign was performed during September 2014 in southern Romania in two different locations: Magurele, Ilfov County and Turceni, Gorj County. This paper presents one case study with analysis of the aerosol properties from in-situ, passive remote sensing and active remote sensing measurements. A Multiwavelength Raman Lidar (RALI) provided one hour averaged vertical profiles of extinction and backscatter from the 532 nm and 1064 nm channels in Magurele. The UV scanning Lidar (MILI) provided one hour averaged backscattered and extinction vertical profiles for Turceni. Planetary Boundary Layer Height (PBLH) was calculated using the altitude of the maximum negative gradient of the range corrected signal. Mass concentrations for different aerosol species (organics, nitrate, sulphate, ammonium and chloride) were obtained from in-situ measurements using Aerosol Mass Spectrometer located in M·gurele and Aerosol Chemical Speciation Monitor (ACSM) located in Turceni.

Keywords: Lidar, sunphotometer, ams, acsm, pbl, campaign

Some of the major stressors of air quality in the urban areas are nitrogen oxides, ozone and suspended particles [1]. Air pollution in Romania is one of the important subjects studied in the last years (e.g., [2-4]).

An air quality monitoring campaign was performed in Romania during September 2014 in two locations. The first one, i.e., Magurele is a suburban location outside Bucharest, in the southern region. The second location, Turceni, is approximately 290 kilometres West of Bucharest. Near the city of Turceni, is the Turceni power plant, which is the Romanian largest electricity producer and one of the largest power plants in Europe.

This paper presents a one day data analysis during the campaign from both Magurele and Turceni sites. Aerosol backscatter and extinction profiles are analysed using one Lidar system for each of the location, Raman Lidar for Magurele (RALI) and UV scanning Lidar (Mili) for Turceni. From both systems, the planetary boundary layer height is retrieved using the gradient method on the range corrected signal. Aerosol mass and size distribution was retrieved using the C-ToF Aerosol Mass Spectrometer (AMS) at Magurele and Aerosol Chemical Speciation Monitor (ACSM) in Turceni [5] have used this approach for characterization of biomass burning aerosols.

A sunphotometer was used to retrieve the Aerosol Optical Depth (AOD) and the Angstrom Exponent (AE) in Magurele and for the Turceni different ground level gas species concentrations were available using the gas analysers HORIBA 250 and HORIBA 270.

The purpose of this study is to assess air quality (both aerosols and gases), considering also synoptic conditions and air mass influences in two high polluted locations based on in situ measurements, remote sensing techniques and satellite imagery.

Experimental part

Instruments and methodology

Lidar systems (MiLI and RALI)

Two active remote sensing instruments were used during this campaign: the UV scanning Lidar – MILI (in Turceni) and the multiwavelength Raman Lidar –RALI (in M·gurele). First one uses a Nd:YAG laser and emits his third harmonic at 355 nm, having a repetition rate of 20 Hz with a 20 mJ energy. The incoming photons are collected with a 200 mm Cassegrain telescope and the system acquisition is analog and photon counting. The system has the full overlap at 200 m and a spatial resolution of 7.5 m but the zenith angle can be modified. The multiwavelength Raman Lidar uses three emission wavelengths, the 1064 nm, 532 nm and the 355 nm with a total emitting energy of 330 mJ and a repetition rate of 10 Hz. The backscattered radiation is collected with a 400 mm diameter Cassegrain telescope. The system detects the three emitting wavelengths, 1064 nm, 532 nm, 355 and two N_2 Raman channels at 387 nm for 355 nm and 607 nm for the 532 nm channel. The system overlap is at about 500 m [3].

The backscattered profiles from the 532 nm channel and 355 nm channel were investigated using the Fernald – Klett algorithm with constant Lidar ratio (assumed) [6]. For the Lidar ratio, the assumption is with 10-15 sr uncertainty, depending on the temporal differences between Lidar and sunphotometer measurements. The vertical profiles are 1 h averaged and the error is calculated using the propagation of the statistical error through the calculus chain.

From the Range Corrected Signal (RCS), which has a temporal resolution of 1 minute, the PBLH is retrieved. It is calculated from the altitude of the maximum negative gradient of the range corrected signal from the 532 nm channel [7]. For every RCS profile, 5 more negative peaks are considered along with the maximum negative gradient. The valid PBL height point is considered the closest one accordingly to the previous PBL height point.

ACSM and AMS

In this campaign, two similar spectrometers have been used in order to obtain chemical composition of submicronic non-refractory species for each site: Time of Flight Aerosol Mass Spectrometer (C-ToF AMS) located in Magurele and Aerosol Chemical Speciation Monitor (ACSM)

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located in Turceni. Both instruments analyze particles with diameter smaller than 1 micron, known as PM1 and measure the mass concentration for organic and inorganic (sulfate, nitrate, chloride and ammonium) particles [8], [8, 9]. The operation principle of the AMS and ACSM is based on vaporization of non-refractory aerosols on a heated tungsten surface at 600 °C and ionization at 70 eV of gas plume resulted, more detailed described by [10]. The ion signal is converted into concentration $\mu g/m^3$, with a detection limit for C-ToF AMS, which ranges from 3 ng m^{-3} for nitrate and sulfate to 30 ng m^{-3} for organics and ammonium [11]. The ACSM is more robust, and has a detection limit higher than C-ToF AMS around 0.2μg. m^{-3} for all measured species. Although ACSM does not measure the size distribution, it is better suited for field campaigns because of the smaller size and the simpler operation mode [12].

Sunphotometer

The Sunphotometer is part of the Aerosol Robotic Network (AERONET). It consists of a collimator, several interference filters, and two detectors for the measurement of direct sun, aureole and sky radiance. The incoming radiation is attenuated by atmospheric components. The attenuation is proportional to the amount of aerosol particles. Sky radiance observations are used for inversion algorithms to retrieve microphysical aerosol properties. It is necessary to perform the measurements under varying azimuth and elevation angles in order to get a wide range of scattering angles.

For the Bucharest site, direct sun radiation is measured in seven channels, 340 nm, 380nm, 440 nm, 500 nm, 675 nm, 870 nm and 1020 nm. Sky radiation is obtained in four bands from 440 to 1020 nm. From direct sun measurements the Aerosol Optical Depth (AOD) can be derived along with the Ängström exponent using the Lambert – Beer law.

$$E_\lambda = E_{0\lambda} \exp(-m\tau_\lambda)$$

where E_λ is the measured irradiance, $E_{0\lambda}$ is the extra-terrestrial solar irradiance, τ_λ is the vertical total atmospheric optical depth and m the air mass depending on the solar zenith angle. Ängström exponent is defined as:

$$\tau(\lambda) = \tau_1 \lambda^{-\alpha}$$

where τ_1 is the approximated AOD at a wavelength of 1 μm sometime called the turbidity (Angstrom, 1964), and α is known as the Angstrom exponent.

The inversion of sky radiance measurements within AERONET to obtain microphysical aerosol properties is described in details by several papers [14, 15].

The atmosphere has to be free of clouds in order to get usable results; otherwise, data have to be removed. A cloud – screening algorithm is carried out. It is based on the variability of the optical thickness (depth). Strong variations within a short period indicate rather clouds than aerosols [16]. Several studies have been published using Romanian network of sunphotometers (e.g., [17] and [18])

Gas analysers

The gas analysers measure gas concentrations using classical methods such as the cross-flow modulated semi decompression chemo-luminescence method (for NO_x monitor), UV fluorescence (SO_2 monitor), non-dispersion cross modulation infrared analysis method (CO monitor), ultraviolet absorption method (O_3 monitor), cross-flow modulated selective combustion type method combined with a hydrogen ion detection method (THC monitor) and gas filter correlation spectroscopy (CO_2).

The instruments require periodic zero/span calibrations to ensure the quality of the data. Another issue that could affect the data is related to the instrument response time. According to the measured species, the gas analysers have different response times related to the measurement principle. For the CO monitor, the response time is within 50s at the lowest range (LR), the SO_2 monitor has a response time within 120 sLR, the NO_2, NO monitor has a response of 90 s LR, for the THC monitor the response time is within 60s, and the time response for the ozone monitor is 75s. These response times can affect fast changing concentrations of ambient gas detected by the instrument.

The primary parameters measured by these instruments are the concentration of one or several gas species within the ppb-ppm range namely, CO (0-100 ppm), SO_2 (0-0.5 ppm), NO, NO_2 (0-1 ppm), CH_4, NMHC, THC (0-50 ppm), O_3 (0-1 ppm). In Romania, a detailed analysis of data recorded at EMEP mountain sites was published in [4].

For each measured component, the system provides four types of data: momentary values, integrated values, moving averages, and simple average. The 3 min data is used to calculate the hourly average of gas concentration [2].

The standard deviation of the hourly average (provided from the 3 min time period) is added to the instrument's linearity and span drift specification values to provide a complete systematic and statistical error analysis.

Satellite imagery

Satellite instruments (such as GOME, SCIAMACHY and OMI) use spectroscopy to retrieve atmospheric trace gas concentrations in the atmosphere. By comparing the measured spectrum of the backscattered light from the Earth's atmosphere with a reference spectrum, the column density of nitrogen dioxide along the light path can be determined. The NO_2 stratospheric column is deduced from a chemistry-transport model assimilation run of the NO_2 column data. Subsequently, the assimilated stratospheric column is subtracted from the retrieved total column, resulting in a tropospheric column [19]. NO_2 concentration map over Romania was used in order to compare the results from the satellite with those obtained from in situ data.

Another satellite data used in this paper was the AOD map from Terra/Moderate Resolution Imaging Spectro-radiometer (MODIS), which monitors the ambient aerosol optical thickness over the oceans globally and over a portion of the continents. Further, the aerosol size distribution is derived over the oceans, and the aerosol type is derived over the continents (MODIS).

Results and discussions

Our analysis starts with an overview on synoptic and meteorological conditions that can influence the accumulations of pollutants near the surface was necessary.

During September 9, 2014 according to the synoptic charts of 700 hPa (fig. 1), there was a complex air mass circulation with a north-eastern component over the eastern part of Romania, while over the western half of Romania, the main circulation was southern-south-eastern. For the M·gurele location, aerosol particles have been advected from Eastern Europe (Moldova, Ukraine, East Romania) as it is shown by the backward trajectories (fig. 2 left).

Hysplit backward trajectories [referinta necesara conform cerintelor de citare mentionate in site-ul NOAA Hysplit] ending on September 9 2014 at the lower level of the troposphere (fig. 2 - left) indicate the advection of an

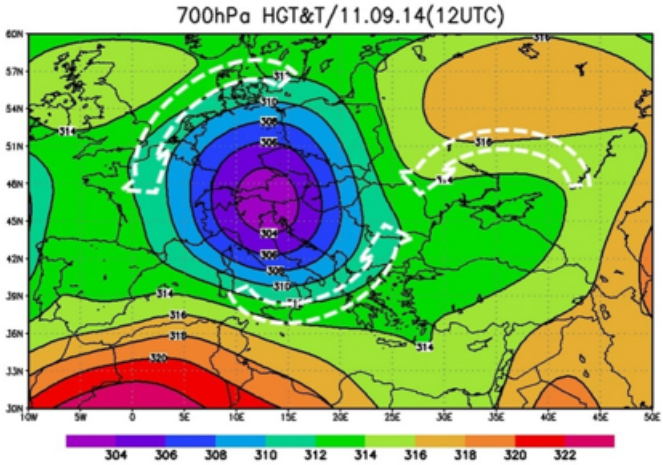

Fig. 1. 700 hPa geopotential height (12 UTC)

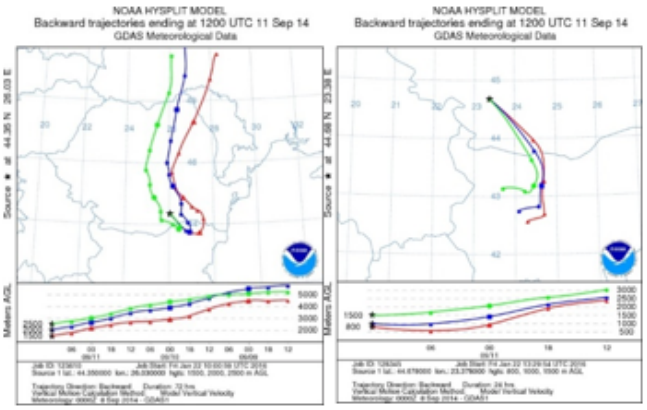

Fig. 2. Hysplit backward trajectories for Magurele (left) and Turceni (right) locations

air mass enriched with fine aerosols originated from Danube area with influence from biomass burning or other continental sources.

The anthropogenic pollution influencing the measurement site is shown by the lower trajectories coming above the Lidar site from Turceni power plant (fig. 2 - right). The ground-based measurements emphasize the presence of local aerosols at Turceni.

In situ measurements

Ground based gas analysers show the presence of a local SO_2 – NO_2 source. The wind direction data at ground level (retrieved from weather station) shows air masses coming from E-ESE during the entire day. SO_2 shows a maximum of 42 ppb at local 10 AM and the NO_2 concentration reaches its maximum of 95 ppb at same local time (fig. 3). The recorded 30 min averaged concentrations are below the standard limits. The gas analysers showed a maximum concentration of hourly averaged NO_2 of 71.45 ± 25.13 ppb and the hourly averaged standard limit is 100 ppb. For SO_2, the maximum hourly averaged concentration is 34±14.35 ppb, while the standard hourly averaged limit is 75 ppb.

High concentrations in NO_2 in this area are influenced by the power plant that uses as main combustion source the coal. Previous studies [20], demonstrate that fossil fuel burning process is responsible for important NO_2 quantities released in the atmosphere.

The significant levels of SO_2 found in the atmosphere is related to combustion source, lignite being one of the main fuel used for power plants in Romania [21]. Lignite is an inferior coal, with low energetic values (1664-2456 kcal/kg) containing an important quantity of sulphur i.e., 1-1.5%.

The aerosol from in situ measurements made in Turceni emphasizes the important contribution of secondary inorganic aerosols that is correlated with increasing of gases concentrations. After 9:00 AM concentration of ammonia and sulfate has an increasing tendency, sulfate having a significant growth from 3 to 9 μg/m^3. These two inorganic components originate from the decomposition

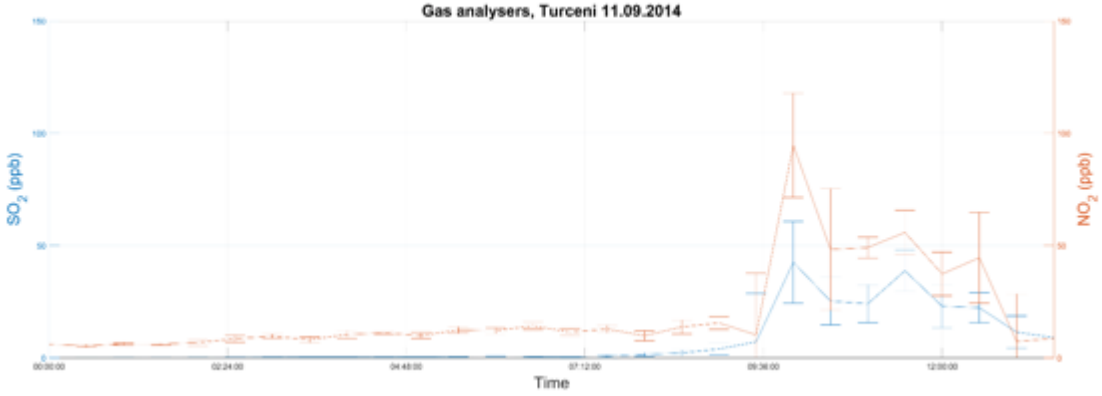

Fig. 3. SO_2 and NO_2 concentration for Turceni location, 11.09.2014

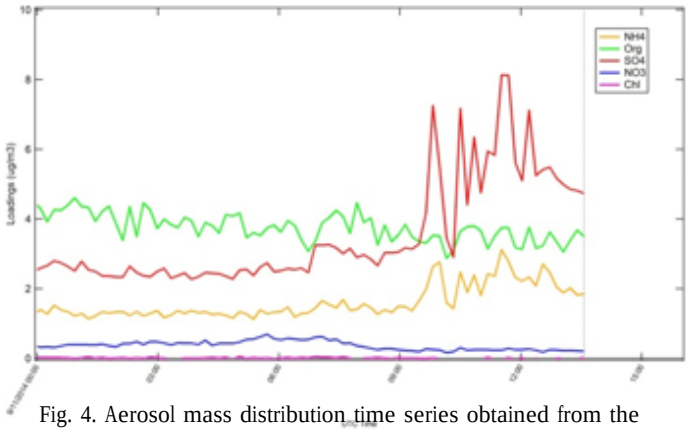

Fig. 4. Aerosol mass distribution time series obtained from the ACSM

of the ammonium sulfate ($(NH_4)_2SO_4$), which is attributed to the anthropogenic sources (fig. 4). The correlation between SO_2 and SO_4 indicates a possible gaze phase to aerosol conversion.

The lack of association between NO_2 and NO_3 as aerosols could be attributed to atmospheric conditions (high temperature 28°C and low relative humidity ~40%) that do not facilitate the transformation from gas to particles.

The measurements made in Bucharest highlight that the organic species have higher concentration than the inorganic components, with a total average of 3.44 μg/m^3. All the compounds have a decreasing trend, except sulphate with higher concentration starting at 9 o'clock.

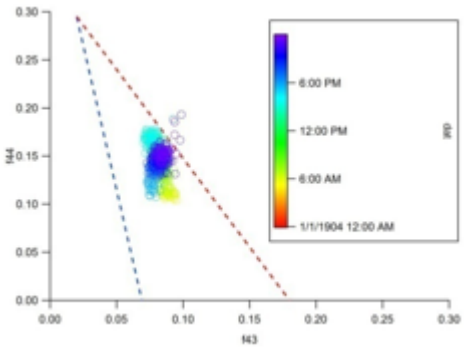

Fig. 5. F43 vs F44 plot from the AMS

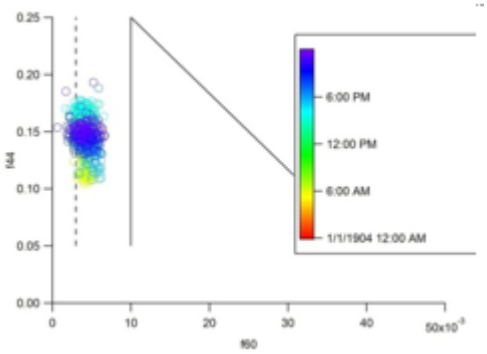

Fig. 6. F44 vs F60 plot from the AMS

From analyses of organic markers, the significant presence of *f44* that is an indicator for the aging of the organic aerosol can be underlined. The values higher than 0.1 revealed the presence of high oxidized particles especially in the second part of the day, while values of *f60* above the background level 0.003 [22] indicated the influence of biomass burning.

Remote sensing measurements

Continuous Lidar measurements were done over M·gurele from 6 AM to 6 PM UTC with the Raman Lidar – RALI, while for Turceni, measurements were performed 3 hours between 8:30 AM to 1:30 PM.

The Range Corrected Signal (RCS) over Bucharest-Magurele (fig. 7) shows a high load of aerosol well mixed within the Planetary Boundary Layer (PBL) after 10 AM UTC, similar with results of [23]. PBLH (marked with the white X*)* starts at around 600 m in the morning and increases up to 3000 m for the rest of the day. Previous measurement days also show an influence of the long range transported aerosols (data not shown).

The PBLH above Turceni is between 700 m and 1200 m as it can be seen in figure 8. PBL height results from Lidar measurements were compared with the results from the European Center for Medium range Weather Forecasting (ECMWF) forecast model, which uses the potential temperature to retrieve the PBL height [24] every 3 h. The results show similar trends for both Turceni and Magurele (data not shown).

Vertical profiles of the extinction coefficient (grey) for the Magurele (fig. 9) show a thin layer of aerosols between 2000 and 3000 m and it is most probably a mixture of

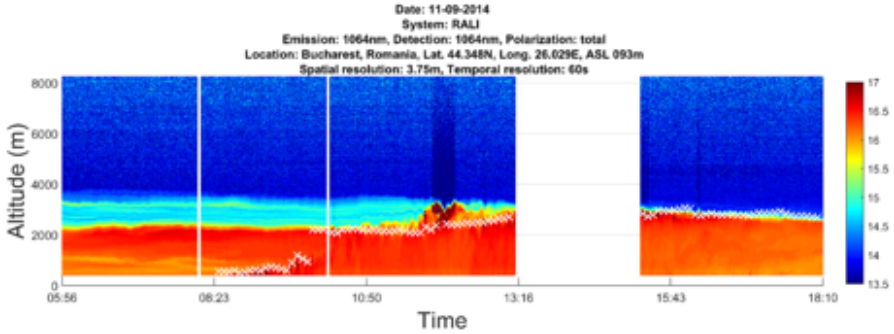

Fig. 7. Range Corrected Signal, RALI, Bucharest - Magurele

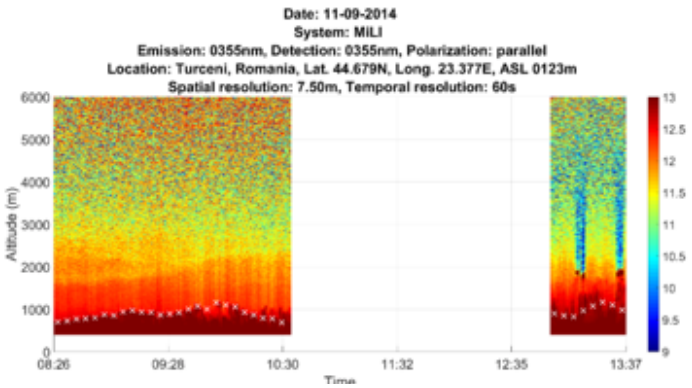

Fig. 8. Range Corrected Signal. MILI, Turceni

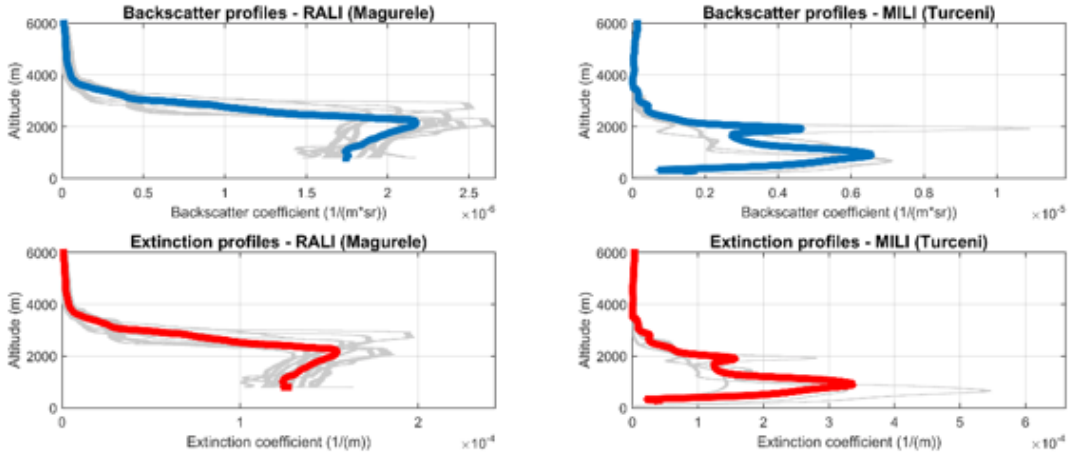

Fig. 9. Backscatter profiles (top row) and Extinction profiles (bottom row) for Magurele (left) and Turceni (right) locations

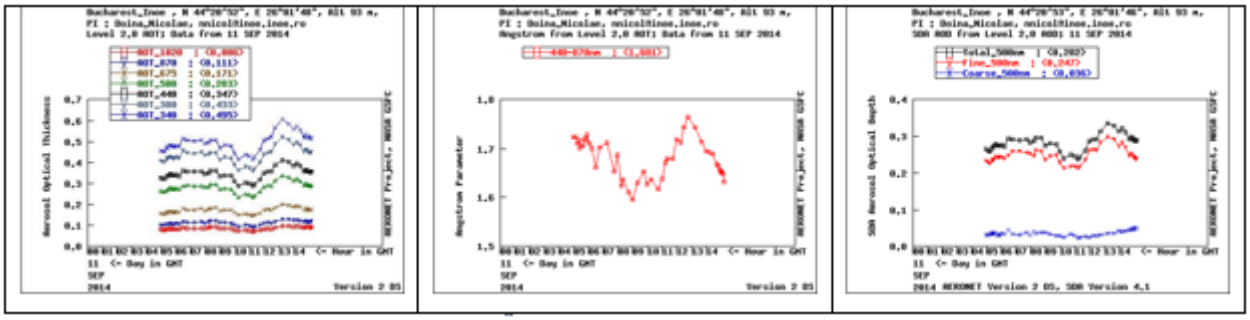

Fig. 10.. Sunphotometer AOD (left), Angstrom exponent (middle) and Fine - course mode distribution (right)

urban pollution and smoke. The overall mean extinction and backscatter profile (blue) shows a high load of aerosols up to 2000 m.

The vertical extinction profiles for Turceni (fig. 9) have larger error bars because the assumption needed to constrain the Lidar profile based on the AOD as explained in the methodology section. There were no sun photometer data available for Turceni, so the AOD was retrieved using data from MODIS.

Sunphotometer data are available only for Magurele and the AOD at 500 nm has an average of 0.283 with a standard deviation of ±0.07. The Angstrom exponent has an average of 1.68 and a standard deviation of 0.20 (fig. 10).

The AOD map from MODIS aboard NASA's Aura satellite (data not shown- available online at: http://giovanni.gsfc.nasa.gov/giovanni/) over Romania shows values around 0.3 agreed with the Sunphotometer who recorded a daily mean of 0.283 with a standard deviation of 0.07 for Magurele.

Conclusions

Trace gases and aerosols were analyzed in two different locations from south Romania using different remote (in situ, passive and active) instruments for September 11, 2014.

In Magurele, the RCS shows an influence of long range transported aerosol, which is mixed within the planetary boundary layer. Hysplit backwards trajectories show influences from the Danube area. The AMS provided the information for the local size and mass distributions of the aerosols. The AOD map over Romanian country from MODIS shows similar values with those retrieved from the Sunphotometer suggesting a good correlation between them.

For Turceni, the Lidar system show no influence from long range transported aerosols. The NO_2 and SO_2 concentrations are significantly higher during daytime. Backward trajectories analysis shows a possible influence from the south region of Turceni. Both results from the ACSM and from the gas analyzers were correlated.

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