Determination of NO_2 amount in polluted air masses over Évora- Portugal, during 2010 with remote sensing measurements

Ana F. Domingues[1], Daniele Bortoli[2], Ana Maria Silva[3]

Abstract — This study provides information about nitrogenous (polluted) air masses transported over Évora, in 2010, detected with a ground based UV-Vis Spectrometer installed at the Geophysics Centre of the University of Évora (CGE). The SPATRAM (Spectrometer for Atmospheric Tracers Measurement) performs measurements of the diffused solar radiation through a vertical path in different spectral intervals (200 - 900nm). The application of the DOAS (Differential Optical Absorption Spectroscopy) methodology to the SPATRAM spectral data, allows for the determination of the total columns of the atmospheric compounds presenting absorption features in the analyzed spectral intervals. The joint action of the SPATRAM data and HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) maps, allows for the identification of the sources responsible for the pollution events recorded at the Évora Observatory. Using the above methodology 71 days in 2010 with pollution events were found. The potential sources of NO_2 that were identified are mainly in Portugal (Lisbon and Tagus Valley and Sines) but there are also sources in Spain and very few sources in North of Africa. For the days in which pollution events were identified, a quantitative study is also presented where the amount of NO_2 over Évora is determined.

Keywords — nitrogen dioxide, remote sensing, air pollution, spectrometer

1 Introduction

Many of the global environmental changes forced by human activities are mediated through the chemistry of the atmosphere. Important changes include the global distribution of air pollution, stratospheric ozone depletion, global warming and increases in the concentration of tropospheric oxidants. Since the agricultural and industrial revolutions the fragile balance between physical, chemical and biological processes in the Earth System has been perturbated as a result of the increase in the world population, the massive use of large amounts of fossil fuel and the related emissions of polluted gases to the atmosphere, and the intensification of agricultural practices including the more frequent use of fertilizers. The anthropogenic contribution of atmospheric emissions to the atmosphere leads to the increasing abundance of some atmospheric compounds like NO_x, O_3, CO_2, CH_4. Currently, some of those pollutants are measured at different ground-based stations with in-situ and/or remote sensing instruments. The increasing interest on the study of atmospheric pollutants is mainly due to their adverse effects on health and ecosystems [1], [2].

In this context air pollution has become one of the major environmental issues and has become a very important factor to the maintenance the urban air quality. Air quality in cities is the result of a multipart interaction between and natural and anthropogenic environmental conditions [3].

A major likely reason for the air quality problems is urban population growth combined with change in land use due to increasing urban areas [3]. The urban population growth has many consequences like the higher emissions of air pollutants. These emissions can be categorised as a) motor traffic, b) industry, c) power plants, d) trade and e) domestic fuel [4]. Nevertheless the motor vehicle traffic seems to be the most important source group for air pollution especially in cities. As cities expand the number of motor vehicles increase and more people buy a car and travel in it much longer than before and over greater distances.

The process of air pollution works as follows: gases and particulate pollutants emitted into the atmosphere are diluted or dispersed by air movements that carry them away from the initial source and diffuse them into larger volumes of air by turbulent eddies [4]. Those gases and particles in the atmosphere can affect the populations locally as well as at distant places from the sources and in a more or less permanent way causing health problems. The exposure to NO_2 has been associated with an increase in respiratory infection and wheezing [5].

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The aim of this study is the use of the ground-based spectrometer SPATRAM installed at Évora to identify and characterize some sources of the episodes of air pollution (in terms of high loads of NO_2) reaching the city.

2 NITROGEN DIOXIDE

Nitrogen dioxide is one of the most important species in tropospheric chemistry because it plays a fundamental role in it.

NO_2 atmospheric chemistry controls in part the oxidizing capacity of the troposphere, as well as the abundance of tropospheric ozone. In fact the photolysis of NO_2 leads to a photochemical formation of ozone during daytime by a catalytic cycle involving organic peroxy radicals (RO_2), the hydroperoxy radical (HO_2), the hydroxyl radical (OH), volatile compounds (VOC) and carbon monoxide (CO). NO_2 can also react with O_3 to form nitrate radical (NO_3), which is a strong oxidant and plays an important role in nighttimes chemistry. The main products of NO_2 in the troposphere are peroxyacetyl nitrate (PAN- $CH_3C(O)OONO_2$) and nitric acid (HNO_3). Nitric acid is produced by daytime reaction of NO_2 with OH radical or by night time formation of N_2O_5 followed by hydrolysis on aerosols [6]. All the chemistry of NO_x can be found in literature [7], [8:33], [9:7, 8, 15-18], [10]. The NO_2 can also modify the Radiative Balance of the Earth trough its influence not only on the tropospheric ozone chemistry but also on the lifetimes of methane and other greenhouse gases. In addition nitrogen dioxide can act as an acidifying and eutrophysing agents in terrestrial ecosystems trough dry or wet deposition of its oxidation products [6].

The abundance of NO_2 in the troposphere is highly variable and influenced by both anthropogenic and natural emissions [11]. On a global scale, the major sources of NO_2 and NO (NO_x = nitrogen oxides) are fossil fuel combustion, biomass burning, lightening and soil microbial production, the oceans, the input for stratosphere and the oxidation of ammonia in the atmosphere [7].

Tropospheric NO_x has a relatively short lifetime on order of hours in the boundary layer and a few days in the upper troposphere and is usually considered to be confined to polluted areas [6]. Nitrogen dioxide is a major problem in urban areas representing an important urban pollutant in most of European cities. The nitrogen compounds especially the NO_x compounds play a very important role in atmospheric chemistry and for formation of photochemical oxidants (O_3, NO_2, nitrates and PAN) many of these compounds act as irritants on the respiratory tract of humans and may also lead to chronic diseases. Road traffic is the main source of nitrogen oxides in urban areas in most of large cities all over the world [11]. Nitrogen oxides are formed under combustion at high temperatures in petrol as well as diesel engines. The emission of nitrogen oxides from road traffic is typically less than 50 % of the total emission, but because the emission from vehicles occurs near the ground, in contrast to the emission from power plants and industries the road traffic contributes up to 90% of the concentration in urban air [11].

Most of the nitrogen oxides are emitted to atmosphere as NO, which is believed to be harmless in the usual concentrations even in heavily polluted cities [11] and the remaining part is mainly NO_2. Concerns over the health impacts lead to the EU First Daughter Directive (99/30/EC) which sets an annual mean limit of 40 $\mu g/m^3$, and a hourly limit of 200 $\mu g/m^3$ that must not be exceeded on more than 18 occasions each year [12], [13].

3 INSTRUMENTAL SETUP AND METHOD

The SPATRAM instrument, Fig. 1, is a multipurpose UV-Visible spectrometer that is currently used to carry out measurements of the zenith scattered radiation (or in passive mode") in different spectral intervals (10 windows of 60 nm each, in the range 250-900 nm with a typical spectral resolution from 0.3 nm at 250 nm to 0.9 nm at 950 nm), to retrieve the vertical content and profiles of some trace gases like O_3 and NO_2 being capable of performing air quality monitoring.

The spectrometer was developed by the Atmospheric physics group of the Geophysics Centre of the Évora University (CGE-UE) in collaboration with the Institute for Atmospheric Sciences and Climate of the National Research Council (ISAC-CNR) in Italy and the Italian National Agency for New Technologies, Energy and the Environment (ENEA). The SPATRAM is installed at the Observatory of the Geophysics Centre of Évora (38.56N, 7.90W) for seven years now. More details about the SPATRAM instrument can be found in literature [14], [15], [16].

Fig.1. The SPATRAM installed at the Observatory of the Geophysics Centre of Évora (38.56N, 7.90W, 300 a.s.l.).

The spectral data gathered by the SPATRAM is processed with DOAS technique for all sky conditions, for the retrieval of the slant column density (SCD) of NO_2. In this particular case the

wavelength range 428,3–460,5 nm was selected, where there is a strong absortion band due to NO_2. The DOAS methodology is based on the DOAS Master Equation (Eq. 1) that is the differential form of the Lambert– Beer law [14]:

$$\log\left(\frac{I_0(\lambda,\theta_{\min})}{I_s(\lambda,\theta)}\right) - \overline{\log\left(\frac{I_0(\lambda,\theta_{\min})}{I_s(\lambda,\theta)}\right)} = \Sigma_g\left(\sigma_g(\lambda) - \overline{\sigma_g(\lambda)}\right)SCD_g(\theta) \quad (1)$$

where $I_0(\lambda,\theta)$ is the reference spectrum obtained at local noon, $I_s(\lambda,\theta)$ is the twilight spectrum, $\sigma_g(\lambda)$ are the absorber's cross sections, θ is the solar zenith angle, $\theta_{\min}$ is the solar zenith angle reached at the local noon and $SCD_g(\theta)$ are the slant column densities of the g^{th} absorber (in this case NO_2). The over - striking notation is adopted to identify the smoothed terms allowing for the removal of the Fraunhofer lines of the solar spectra. The smoothing operator is obtained with the Fast Fourier Transform Algorithms [17]. The normalized difference between the absolute spectral series and the filtered one is referred to as the 'differential' spectrum. The differential spectrum is compared with the atmospheric trace gases under investigation, by means of the 'differential cross section' ($\sigma_g(\lambda) - \overline{\sigma_g(\lambda)}$) which present measurable absorption features in the selected spectral range in order to retrieve the Slant Column Density ($SCD_g(\theta)$).The spectral evaluation consists of a least squares fit procedure where differential cross sections of the absorber (NO_2 in the present case) are adjusted to the differential log-ratio of a twilight spectrum and a reference one. The description of DOAS methology can be found in literature [18],[19].

The output of SPATRAM is the Slant Column Densities (SCD) of the studied trace gases which indicates the trace gas concentration integrated along the light path in molecules/cm^2. These results are used in studies mainly focused on the air quality monitoring and the environmental pollutions problems [20],[21],[22], [23].

The Air Mass Factor (AMF), representing the average solar photon slant path through the atmosphere, has to be determined by means of a Radiative Transfer Model using the Atmospheric Model for Enhancement Factor Computation (AMEFCO) [23], allowing for the determination of the vertical content density (VCD) of the analyzed atmospheric compound. This Radiative Transfer Model is based on a single scattering approach and an a priori assumption on the vertical NO_2 profile [14].

The VCD is defined as the trace gas concentration integrated along the vertical path trough the atmosphere. In order to obtain the VCD of the compounds under investigation, the Eq.2 has to be applied to the SCDs [16],[24]

$$VCD_g = SCD_g(\theta) / AMF_g(\theta) \quad (2)$$

This quantity does not dependent on the solar position nor of the instrumental line of sight, and is defined as the trace gas concentration, integrated along the vertical path through the atmosphere, usually labeled as 'total ozone column'.

The used methodology combines the SPATRAM data (NO_2 SCDs) to the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) - *at* http://www.arl.noaa.gov/ready/HYSPLIT- 24 hours back-trajectory's at different altitudes (1000m, 3000m, 5000m, 10000m, 15000m and 25000m). The period under investigation is 1 st January to 31st December of 2010. This association allows for the recognition and identification of the potential sources responsible for the pollution events recorded at the site Évora

Évora can be considered as a continental rural location situated in the interior and south of Portugal, having low or very low pollution load levels. Évora surrounding areas are also mainly rural. In the West direction, are located very large urban and industrial areas as Lisbon, Setúbal, Barreiro, Seixal e.g., and in the East direction is situated Badajoz which is an important Spanish city known for its large urban and industrial development. Due to the fact that Évora is considered an "unpolluted" city allows for the detection of unexpected variations in the diurnal NO_2 cycle derived from the NO_2 SCDs obtained with SPATRAM. The identification of potential pollution sources is related to the high possibility of an intrusion of a polluted air mass rich in NO2 into another with low concentration in this particularly gas on urban and industrial sites that travels from the pollution site to the Évora site.

Whenever a variation in the normal behavior of the NO_2 SCD tendencies was detected (a demarked peak), that peak was pointed as one 'pollution event', meaning that an event of tropospheric pollution occurred during the day, at a distant site. The event is marked as 'tropospheric', although SPATRAM, measuring in the zenith sky configuration (pointing to the vertical direction), is most sensitive to the stratospheric content of NO_2 since the bulk of NO_2 is located at 25-27 Km of altitude. However, high loads of tropospheric NO_2 content can be detected by the SPATRAM instrument.

4 RESULTS AND DISCUSSION

Using the above methodology 71 days in 2010 with pollution events were identified. In thirty of those days were registered two or three demarked peaks that were considered as 2 or 3 pollution events. In the other 41 days there was registered only one demarked peak correspondent to only one pollution event.

The potential air pollution sources registered were from sites mainly in Portugal. It was also identified possible pollution sources from Spain and North of Africa.

The next examples illustrate some of the results obtained with the SPATRAM instrument with the application of the above mentioned methodology.

The following example illustrates the pollution event detected in Évora with potential sources in Lisbon and Tagus Valley area.

Fig. 2 shows that near 01:30 PM, 02:00 PM, 03:00 PM and 06:30 PM there are demarked peaks on the NO2 SCD daily concentration obtained with SPATRAM measurements. Analyzing the 24 hours HYSPLIT back-trajectories (Fig. 3) for the same day, for example for the 02:00 PM it can be seen that, at different altitudes, the air mass is passing over high polluted industrial and urban areas like Setúbal (5000 m) , Barreiro, Montijo, Seixal (1000 m), Lisboa area (1000 and 5000 m) (Fig. 4). Apart from being a high populated and industrial region there are also power plants (Alto do Mira- near Amadora, Setúbal and Barreiro) that release also NO_2 to atmosphere.

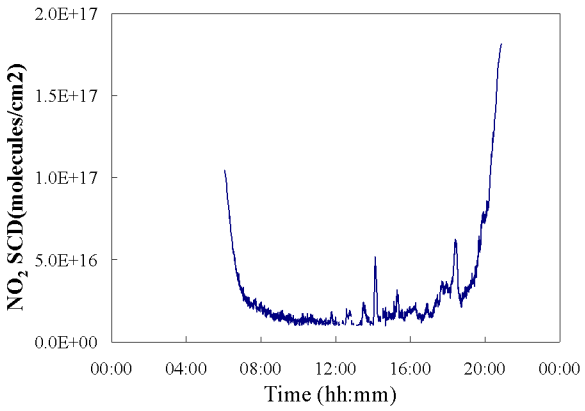

Fig. 2. The NO_2 Slant column densities (SDC) daily variation during 11th May of 2010 retrieved by SPATRAM at Évora.

The NO_2 quantity measured at Évora site for the 02:00 PM event was 0.1901 µg/m^3 (approximately 3.78E16 molecules/cm^2).

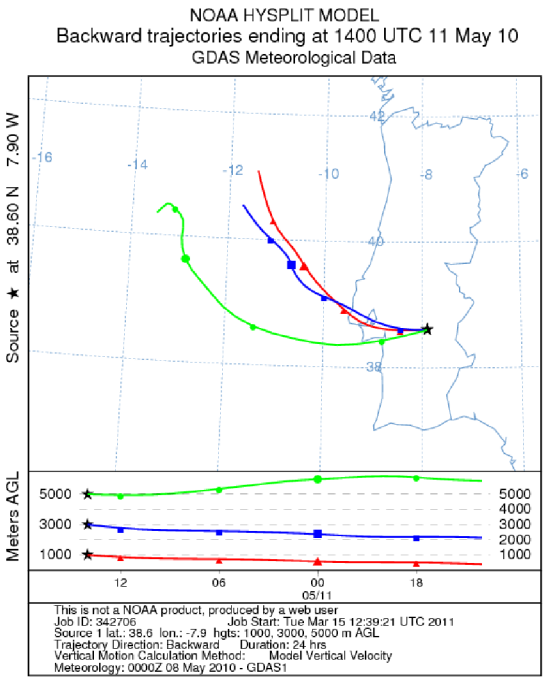

Fig. 3. The HYSPLIT back-trajectories for the 11th May of 2010 at the heights of 1000, 3000 and 5000 m (at http://ready.arl.noaa.gov/hysplit-bin/trajtype.pl?runtype=archive).

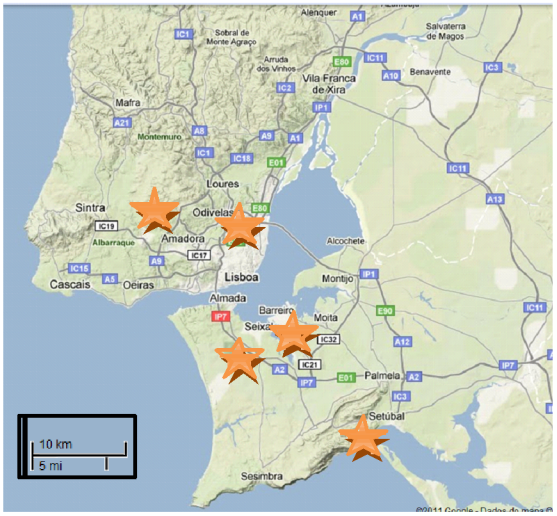

Fig. 4. Location of the potential pollution sources (Setúbal, Barreiro, Seixal, Lisboa, Amadora) detected by the combination of SPATRAM data and HYSPLIT back-trajectories for the 11th May of 2010 at the heights of 1000, 3000 and 5000 m- *at* www.maps.google.com.

The frequency of pollution events occurrence with potential sources in Portugal, during 2010, is summarized in Fig. 5.

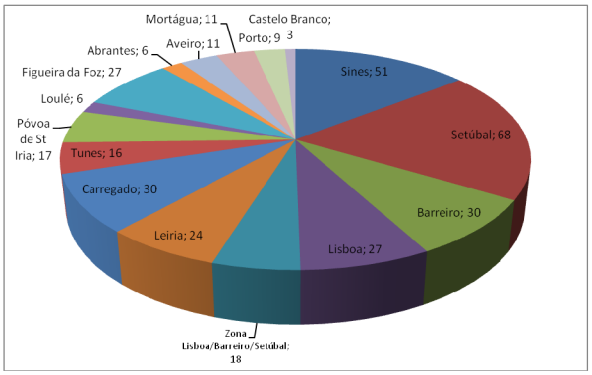

Fig. 5. Number of pollution events registered at Évora's Observatory in 2010 with the potential sources located in Portugal.

The above identified sites are the locations of power plants (Barreiro, Setúbal, Carregado, Póvoa de Santa Iria, Abrantes, Tapada do Outeiro near Porto, e.g.), biomass stations (Vila Velha de Rodão near Castelo Branco e.g.), industrial units (Leiria sorroundings, Lisboa, Porto, e.g.)) and concrete factories (Setúbal, Loulé, e.g.)

Other cases of atmospheric pollution originated in Spain and Morocco were also identified. The next example shown in Fig. 6 is related to a pollution event occurred in the north of Spain and Portugal.

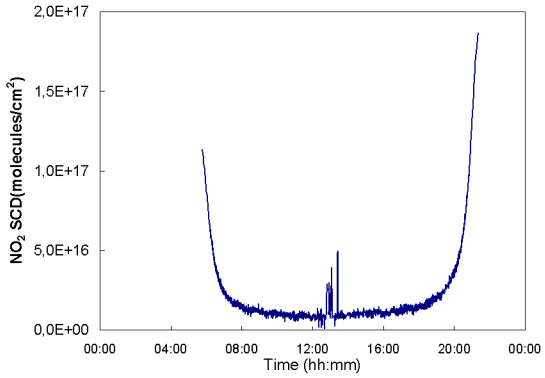

Fig. 6 . The NO_2 Slant column densities (SDC) daily variation during 12th June of 2010 retrieved by SPATRAM at Évora.

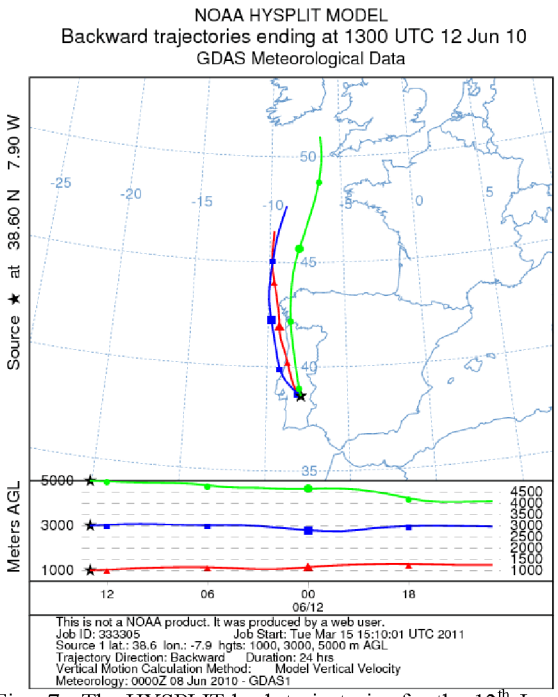

Fig. 7. The HYSPLIT back-trajectories for the 12th June of 2010 at the heights of 1000, 3000 and 5000 m (at http://ready.arl.noaa.gov/hysplit-bin/trajtype.pl?runtype=archive)

The load of NO_2 was identified at Évora Station at 01:04 and 01:24 PM. The most probable NO_2 sources are identified in Leiria (3000m), Figueira da Foz (3000 m), Aveiro (1000, 1500m) and Porto (1000, 1500m) all in Portugal and in Vigo (5000 m) and Coruña (5000m) in Spain with the help of HYSPLIT maps (Fig.7).

The NO_2 loads derived from the SPATRAM scattered radiation measurements were, at 01:04 and 01:24 PM respectively, 0.158µg/m^3 (approximately 2.973E16 molecules/cm^2), 0.216 µg/m^3 (approximately 4.241 E 16 molecules/cm^2).

There are also records of air pollution event from Oviedo and San Sebastian, Salamanca and Madrid in the North of Spain that correspond to urban centers, industrial sites and location of oil refineries and power plants. Cities like Badajoz, Sevilha, Huelva, Cadiz and others like Portullano, Alicante, Córdoba, Cáceres, Gibraltar, Almendralejo, Murcia, Valência, and Cartagena were also identified as potential NO_2 sources.

The following situation (Fig. 8 and Fig.9) illustrates one case where it is possible to observe an air mass motion reaching Évora originated in South of Spain and in North of Africa, namely in Rabat and Casablanca known by the intense road traffic.

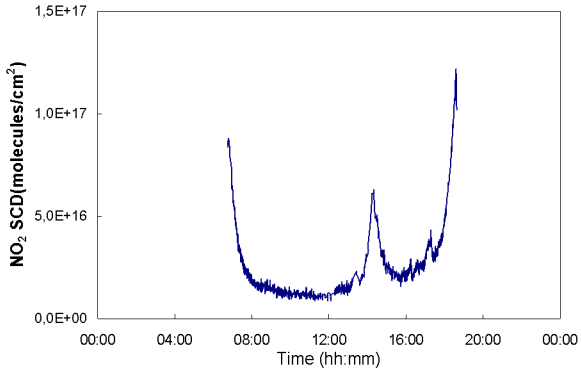

Fig. 8 . The NO_2 Slant column densities (SDC) daily variation during the 2nd of March 2010 retrieved by SPATRAM at Évora.

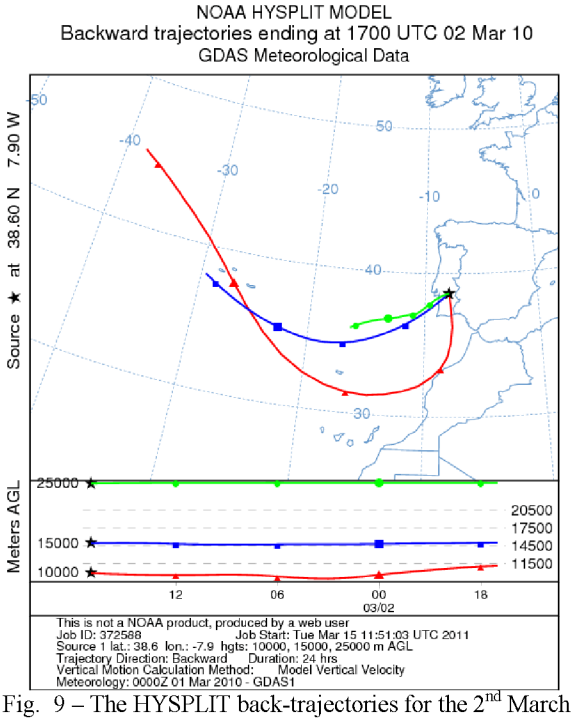

Fig. 9 – The HYSPLIT back-trajectories for the 2nd March of 2010 at the heights of 10000, 15000 and 25000 m (at http://ready.arl.noaa.gov/hysplit-bin/trajtype.pl?runtype=archive)

For the same day it is also possible to identified intrusion of NO_2 air masses from Tunes (5000 and 3000 m) Portimão and from Huelva and Cadiz (1000m). Fig. 10 exhibits the air mass back-trajectories ending at Évora and originated in the above industrial areas (power plant, urban traffic and refineries stations).

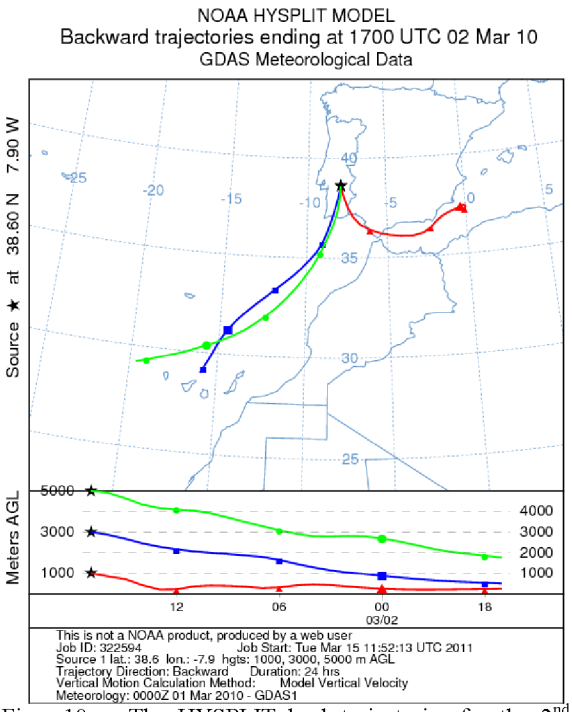

Fig. 10 . The HYSPLIT back-trajectories for the 2nd March of 2010 at the heights of 1000, 3000 and 5000 m (at http://ready.arl.noaa.gov/hysplit-bin/trajtype.pl?runtype=archive).

The total contribution of the above sites that was detected by the SPATRAM was 0.159 $\mu g/m^3$ (approximately 3.89E16 molecules/ cm^2).
In the North of Africa there were also identified other sources of NO_2, like El Jadida (1 event), Tanger (2 events) and Algecira (1 event).

Fig. 11 summarizes the number of occurrences and the potential sources of NO_2 located in Spain.

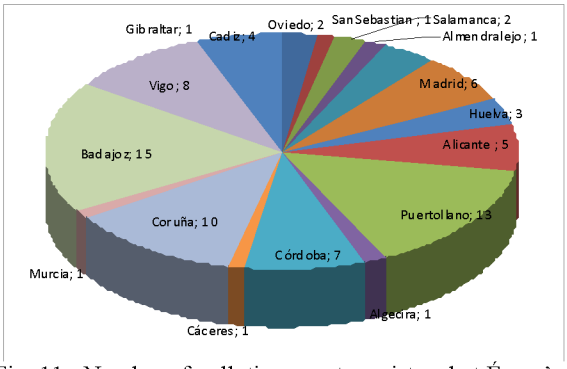

Fig. 11. Number of pollution events registered at Évora's Observatory in 2010 with the potential sources located in Spain.

The nitrogen pollution loads were simply calculated as the differences between the maximum value for each registered event and the background values extrapolated by the regular function described by the daily SCDs. In Fig. 12 is shown the number of events with NO_2 concentration between 0.03 and 0.28 $\mu g/m^3$ (9 bins of 0.03 $\mu g/m^3$ each) that were retrieved by the SPATRAM.

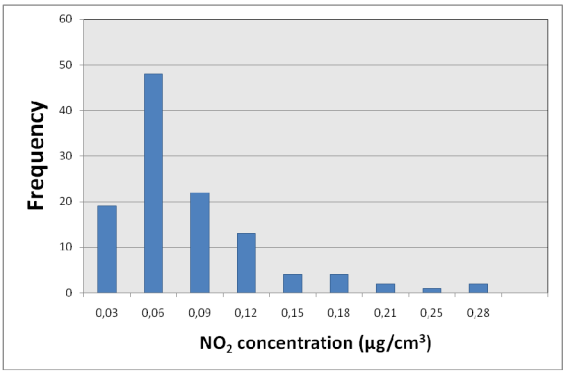

Fig. 12 . Histogram that illustrated the quantity of NO_2 detected in Évora in µg/m^3 with the SPATRAM instrument for each pollution event, for the 115 events recorded at Évora Station.

For the analysis of Fig.12 one can conclude that 48 events were registered where the NO_2 concentrations are between 0.03 and 0.06 µg/m^3, 22 events where the NO_2 concentrations are between 0.06 and 0.09 µg/m^3, 19 events where the NO_2 concentrations are between 0 and 0.03 µg/m^3 and 13 events with NO_2 values between 0.09 and 0.12 µg/m^3. On the other 13 events the NO_2 concentrations lay between 0. 12 and 0,28 µg/m^3. The maximum value obtained in a pollution event occurred in 9 th May 2010 from the SPATRAM scattered radiation measurements reached 0.251 µg/m^3 (approximately 5.133E16 molecules/cm^2) and the minimum value of 0.011 µg/m^3 (approximately 0.94E16 molecules/cm^2) was registered in the 2nd February 2010.

8 CONCLUSIONS

Trough the combination of the column content of atmospheric pollutants (such as the NO_2), obtained from the absorption spectra of these pollutants measured with the UV-Vis SPATRAM), with the 24 hours back-trajectories ending at Évora at different altitudes, given by the HYSPLIT model, it was possible to identify, qualitatively, at the observational site- Évora, several long range as well as short range pollution sources from a wide variety of sites. The main sources of NO_2 pollution that were identified at Évora´s Observatory are located in Lisboa and Tagus Valley and Sines – Portugal – that correspond to urban and industrial sites where Power Plants are placed. There are other sources of pollution related to the NO_2 emissions like the Cogeneration Power Plants located at Leiria, Póvoa de Santa Iria, Lavos-Leiria, the Biomass Centers placed at Vila Velha de Ródão and Mortágua), oil refineries located at Porto, Sines e.g.), industrial units at Sines, Barreiro, Setúbal, Carregado, among other, and the multi sources produced by the heavy traffic existing in the major cities like Lisbon and Porto and in the Great Lisbon and Porto surrounding areas. The above method has also identified long distant NO_2 sources from Spain and Morocco.

In total there 115 pollution events (71 days) were identified at Évora during 2010 where the maximum NO_2 load of 0.28 µg/m^3 was obtained from the SPATRAM scattered radiation measurements.

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