INVESTIGATION OF O_3 ENTRAINMENT AT A NORTH-ITALIAN MONITORING STATION DURING THE PERIOD 2006–2015

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ABSTRACT
High ozone levels at the Earth's surface are known to be harmful to human health as well as vegetation, and the tropospheric ozone also plays an important role in global climate change. Its sources and sinks are, therefore, important to understand. During a 10-year timeframe (2006–2015), entrainment of ozone into the boundary layer was investigated at a regional measuring station in Northern Italy (EMEP/GAW-station, JRC-Ispra, 45.807°N/8.631°E, 223 m above-sea-level), using the *in situ* measurements of air-pollutants, including ozone, meteorological parameters and weekly averaged ^{7}Be and ^{210}Pb activities. The ratio $^{7}Be/^{210}Pb$ was used as an indicator of the contribution of transport from the stratosphere/upper-troposphere to the composition of the air-masses at surface-level. Diurnal variations in ozone, humidity and ^{222}Rn concentrations were used to detect episodes with entrainment of air from the free-troposphere into the boundary layer. Daytime ozone showed a positive correlation to the ratio $^{7}Be/^{210}Pb$ for all years, but with large variations in the correlation coefficient between the years, indicating that the importance of transport from stratosphere/upper-troposphere has large variations from year to year. $^{7}Be/^{210}Pb$ had in this investigation a mono-modal log-normal distribution. Lee et al. (Analyses and comparisons of variations of ^{7}Be, ^{210}Pb and $^{7}Be/^{210}Pb$ with ozone observations at two Global Atmospheric Watch stations from high mountains. *J Geophys Res*, 2007) found a bi-modal log-normal distribution at two high-altitude sites, where the second mode was attributed to episodes of stratospheric-intrusion. Thus, it appears that we do not see, at the low altitude JRC-Ispra station, such clear-cut episodes dominated by stratospheric-intrusions, but a combination of ozone from *in situ* boundary layer photochemistry, tropospheric transport and stratospheric contributions. This conclusion is confirmed by looking at variations of the parameters O_3, humidity and ^{222}Rn, combined with back-trajectories.
Keywords: ozone, natural radionuclide tracers, entrainment, atmospheric pollutants, atmospheric tracers, troposphere, free-troposphere, stratosphere.

1 INTRODUCTION

It is well-known that tropospheric ozone concentrations have increased since pre-industrial times, leading to a positive radiative forcing, because it is a strong greenhouse gas [1], and is also leading to an enhancement of ozone concentrations at the Earth's surface. In addition, high ozone concentrations at the surface are also harmful to health [2], and damage vegetation, reducing crop yields [3], [4].

The two main sources for tropospheric ozone are:

1) Produced *in situ* through sunlight-initiated oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides [5], [6].
2) Stratospheric contributions to the troposphere (intrusions), tropospheric contribution to the boundary layer (entrainment) or other transport processes of ozone rich air masses manly through advection and/or subsidence [7], [8].

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Observations have shown, that in the Mediterranean boundary layer there is an enhancement in summertime ozone, which maximises over the eastern basin of the Mediterranean. The Mediterranean basin during summer-time is largely cloud-free, and the relatively high solar radiation and temperatures in combination with the strong tropospheric subsidence observed in its eastern part, favour high levels of ozone over the Mediterranean area (see e.g. [9]–[13]).

Nearly 30% of the tropospheric ozone over the Mediterranean basin during summer-time is estimated to originate from the stratosphere [7]. In winter this fraction may even be larger [13].

We present here 10 years of data to understand the relative importance of the contributions of the different sources of ozone at a measuring station in the North of Italy (pre-alpine area), in the North of the Mediterranean area.

2 EXPERIMENTAL

The JRC-Ispra site is a regional measuring station in Northern Italy (EMEP/GAW-station, JRC-Ispra, 45.807°N/8.631°E, 223 m above sea-level). At the station in the North of Italy (pre-alpine area), the wind speed is normally rather low throughout the year with occasional Foehn events [14]. The average wind speed for the whole year is typically about 0–2 m s-1. Several parameters were measured in this investigation; they are listed and described in details below:

Ozone was measured continuously and on-line using "Thermo 49 instrumentations" (UV Photometric Ambient Analyzer) during the entire 10 years, except the year 2009 (with an average measuring value every 10 min.). The UV photometer determines ozone concentrations by measuring the absorption of O_3 molecules at a wavelength of 254 nm (UV light) in the absorption cell, followed by the use of Bert-Lambert law. The concentration of ozone is related to the magnitude of the absorption.

^{7}Be and ^{210}Pb measurements were performed at the "site Laboratory for Radioactivity Measurements" (LMR) of the JRC-Ispra, Italy". LMR is in charge for the environmental surveillance network for the Italian JRC nuclear site. Different matrices are collected and measured with the aim to determine any possible contamination originated from the former nuclear installations now been decommissioned. Some environmental radioactive nuclides are also measured. Water, foodstuff, sediment and soil samples are submitted to the low-level radioactivity measurement protocols to quantify alpha, beta and gamma radioisotopes. LMR manages the air collection station placed on the hill outside the border of the JRC (SSW direction). Air is continuously sampled via air pump suction system and filter particulate collection. About 2500 m^3 per week, on yellow 95% efficiency DOP 0.3 mm (the DOP test obtains its name from an abbreviation of the organic material Di-Octyl Phthalate evaporated to create 0.3 micron particles used for this filter efficiency test), is submitted to the gamma measurement after radon decay. GEM series EG&G Ortec High Purity Germanium (HpGe) coaxial detectors are used and expressively calibrated for the filter geometry. The instruments have a thin window carbon fiber of 0.9 mm and 1.8–1.9 keV resolution (FWHM) with 30% efficiency at 1332 keV. ^{7}Be and ^{210}Pb are determined with a decision threshold (a=0.05) of 75 and 150 $\mu Bq/m^3$ respectively [15]. All the data are recorded in LMR "Analisi" LIMS (Polysistem Informatica Srl, Italy).

^{222}Rn activity concentrations have been semi-continuously monitored (30-minute time integration) applying an ANSTO dual-flow loop two-filter detector [16], since Oct. of 2008.

Humidity in units of ppmV of water was calculated from the measurements of RH (Relative Humidity), temperature and atmospheric pressure. A WXT510 weather transmitter from "Vaisala" recorded simultaneously the six measured weather parameters: temperature, pressure, relative humidity, precipitation, wind speed and wind direction at the top of an about 10-m-high mast.

3 RESULTS AND DISCUSSIONS

Data and results were obtained during a 10-year timeframe (2006–2015) to investigate the importance for ground level ozone concentrations of atmospheric subsidence and entrainment of ozone into the boundary layer, at a regional measuring station in Northern Italy.

Episodes were investigated by using the in-situ measurements of air pollutants including ozone, meteorological parameters, ^{222}Rn activities, and finally also weekly averaged ^{7}Be and ^{210}Pb activities.

Some explanations, why the following parameters were used in this investigation:

Ozone: Daily variations in ozone were used to monitor the surface levels and to investigate correlations with other parameters. The 12:00–18:00 averages (local time) were used as they are more representative of boundary layer ozone concentrations due to thermal mixing.

^{7}Be, an atmosphere cosmic-ray-produced isotope (half-life time of 53.22 days), was used as a tracer for transport of air-masses from the stratosphere/upper-troposphere to ground level [17].

^{222}Rn, a uranium-radium series decay product with a half-life time of 3.82 days, is emitted from the surface and is accumulated in the boundary layer. Its concentration thus depends on boundary layer height and mixing within the boundary layer, entrainment of air from the free troposphere will normally result in a decreasing radon concentration at surface level. Its concentration was used to, qualitatively, observe the diurnal variations of the mixing within the boundary layer as well as evidence of impacts of entrainment of air from the free troposphere [17].

^{210}Pb is a daughter's isotope of ^{222}Rn with a half-life time of 22.23 years. The ratio between ^{7}Be and ^{210}Pb was used as an indicator of the entrainment of air originating from higher layers of the troposphere [17].

Humidity: At lower temperatures, the atmosphere can contain less water and consequently the specific humidity decreases with increasing height in the atmosphere. Thus, air that is brought down to the surface by transport from higher altitudes will typically be relatively dry and entrainment of air from the free troposphere is thus often associated with a drop in humidity.

To investigate entrainment episodes plots of ozone vs. ^{7}Be, and of ozone vs. ^{7}Be/^{210}Pb were made for the years 2006–2015, and below are shown some examples from 2011.

Fig. 1 shows daily values of ozone plotted against ^{7}Be for the whole year 2011 and it can, for example, be seen, that in May 2011 and at the beginning of July 2011 there probably was an episode of air-masses coming in from above bringing ozone.

Fig. 2 shows daily values of ozone plotted against ^{7}Be/^{210}Pb for the whole year 2011 and again it can, for example, be seen, that at the beginning of July 2011 there probably was an episode of air-masses coming in from above bringing relatively high levels of ozone to the ground level.

Fig. 3 shows a plot of log(^{7}Be/^{210}Pb) for the entire years of 2006–2015.

Stratospheric ozone intrusions in the Mediterranean take place most frequently in spring and early summer [18], [19]. In the spring, an increase in ozone is also generally seen due to the increasing sunlight intensity. This implies that some caution is necessary in the interpretation of the data as the simultaneous increase in O_3, ^{7}Be and ^{7}Be/^{210}Pb is not

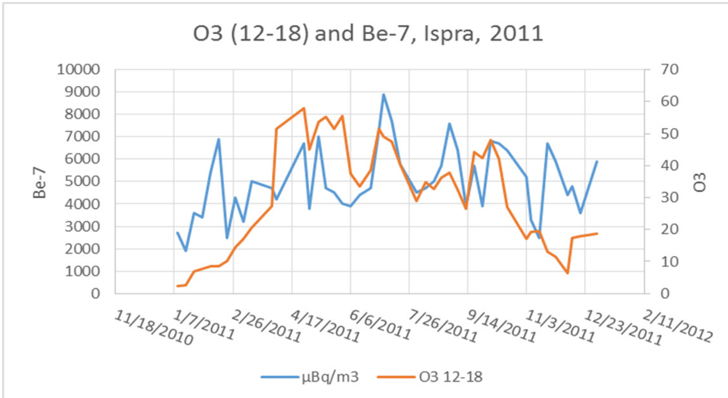

Figure 1: Ozone vs. ^{7}Be the whole year 2011. O_3 in ppbV and ^{7}Be in mBq m^{-3}.

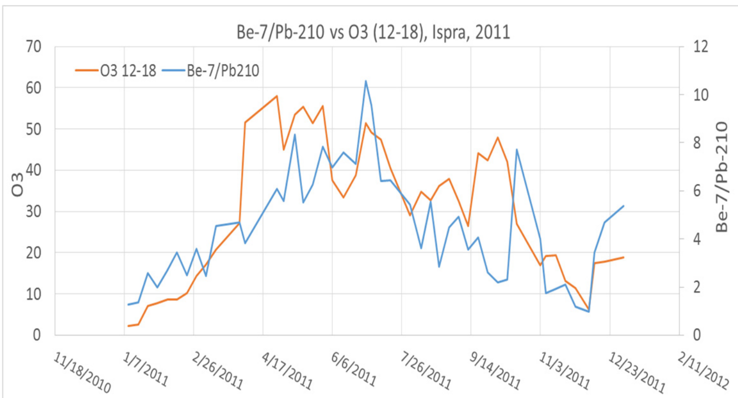

Figure 2: Ozone vs. ^{7}Be/^{210}Pb ratio for the whole year 2011.

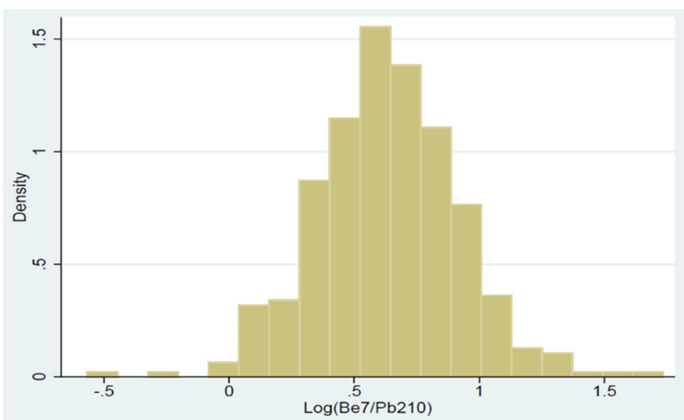

Figure 3: Plot of log(^{7}Be/^{210}Pb) for the entire years of 2006–2015.

necessarily related to the impact of stratospheric intrusions. Thus, the initial increase in ozone and in ^{7}Be and in ^{7}Be/^{210}Pb in the early spring (seen in Figs 1 and 2 respectively) cannot be seen as a clear indication of the impact of stratospheric intrusion. However, the episode during the last week of June 2011 with peak ozone and ^{7}Be/^{210}Pb values as well as the peak values in late May 2011 could be due to stratospheric intrusions, and using back-trajectories for the whole time-frame, could give some answers (in next sections, we actually show that we found several episodes with air-masses from high altitude using back-trajectories for May 2011, and to some extent also for June 2011, but it was not so clear for the end-of-June/beginning-of-July 2011).

The plot in Fig. 3 shows that the frequency distribution of ^{7}Be/^{210}Pb has log-normal distribution. In a previous study [20], a bi-modal log-normal distribution at two high-altitude sites was found, where the second mode was attributed to episodes of stratospheric-intrusions. Thus, it appears that we do not see, at the low altitude JRC-Ispra station, such clear-cut episodes dominated by stratospheric-intrusions, but a combination of ozone from *in situ* tropospheric-photochemistry, transport and stratospheric-contributions.

To finalize this section, we present here the correlations of O_3 (12–18) vs. ^{7}Be/^{210}Pb for the years and for the individual years. The correlation was always positive:

O_3 vs. *^{7}Be/^{210}Pb: Corr. factor y = 2.11 and corr. coeff. R^2 = 0.16 (for all years available)*; y = 2.13 and R^2 = 0.17 (2006); y = 2.31 and R^2 = 0.21 (2007); y = 1.94 and R^2 = 0.29 (2008); y = 1.80 and R^2 = 0.13 (2010); y = 4.74 and R^2 = 0.44 (2011); y = 1.70 and R^2 = 0.13 (2012); y = 3.19 and R^2 = 0.15 (2013); y = 2.44 and R^2 = 0.19 (2014); y = 2.12 and R^2 = 0.11 (2015).

It should be mentioned, that in total, 3 outliers from the data-sets above were removed.

On the next pages, examples are shown for air-masses from above coming in (Foehn, entrainment, intrusion, etc.) and concrete examples from the year 2011 and the year 2013 are taken, including some back-trajectories.

Examples from the year 2011: April 2011 and May 2011: Fig. 4 shows a typical Foehn event (4–5.04.2011), because wind speed was rather high those days and coming from the North (the mountains, average wind speed about 4–5 m s^{-1} with wind speed peak values around 15 m s^{-1}).

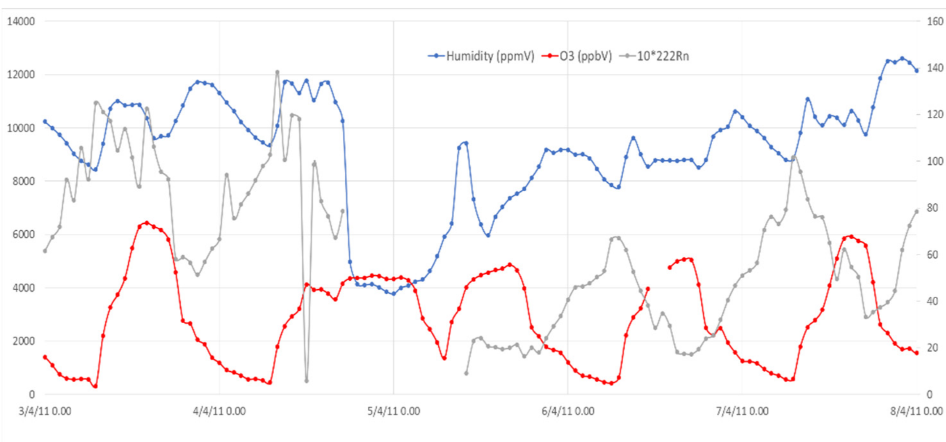

Figure 4: 3–8.04.2011: Plot of humidity (in ppmV, scale left), ^{222}Rn (in Bq m^{-3}, scale right) and ozone (in ppbV, scale right), from JRC-Ispra station, Italy.

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In Fig. 5, episodes with anti-correlations between ozone and humidity (in ppmV) are indicated by arrows. In addition, in Fig. 5 it can be seen that around 05.05.2011, there were also an episode, and here back-trajectories from Fig. 6 actually confirm that air-masses from high altitude were coming down.

HYSPLIT back trajectories were calculated for episodes where simultaneous increasing ozone and decreasing humidity (in ppmV) were observed during the year 2011. Some examples are shown in Fig. 6. When a strong anti-correlation between humidity and ozone is observed, back trajectories show evidence of subsidence (air-masses moving downwards), e.g. for 05.05.2011.

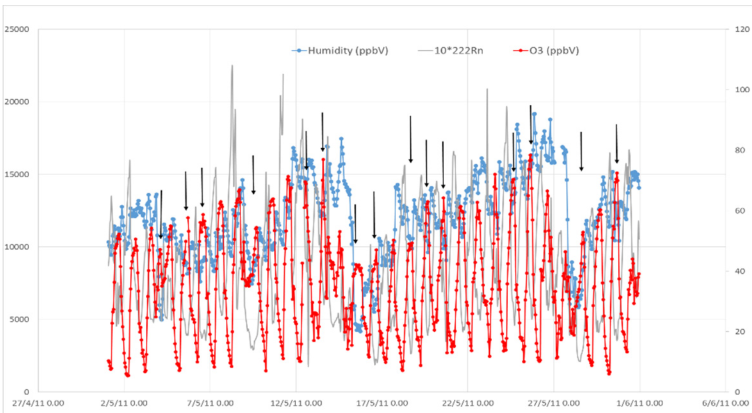

Figure 5: May 2011: Plot of humidity (in ppmV, scale left), ^{222}Rn (in Bq m^{-3}, scale right) and ozone (in ppbV, scale right), from JRC-Ispra station, Italy.

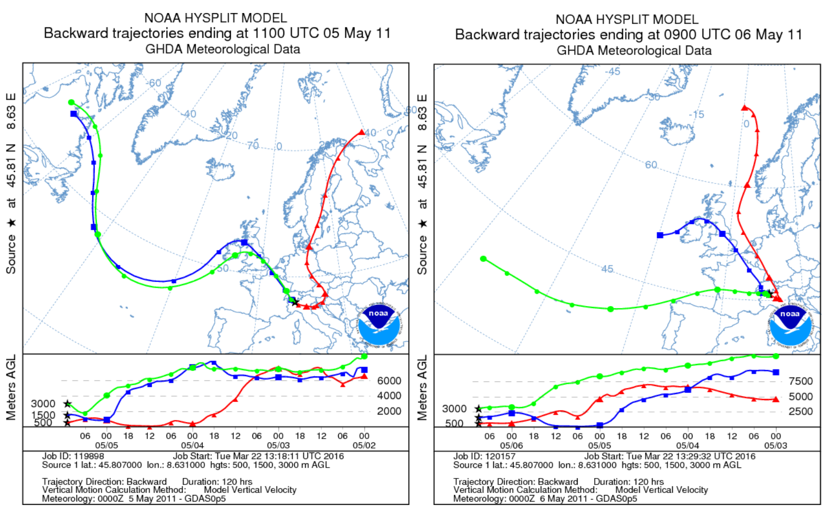

Figure 6: Examples of Hysplit trajectories from year 2011 (*http://www.ready.noaa.gov/HYSPLIT_traj.php*).

Example year 2013, May 2013: An episode shown in Fig. 7 (11–13.05.2013) and Fig. 8 (the whole month of May 2013) we do not attribute to a Foehn event, because wind speed was rather low on these days (wind speed average about 1–2 m s^{-1} with wind speed peak values around 3–5 m s^{-1}, and wind directions on those days in May 2013 were coming from all directions). So the episode in Fig. 7 (11–13.05.2013) is probable an entrainment episode of air-masses from free-troposphere, which is also supported with back-trajectories (shown in Fig. 9).

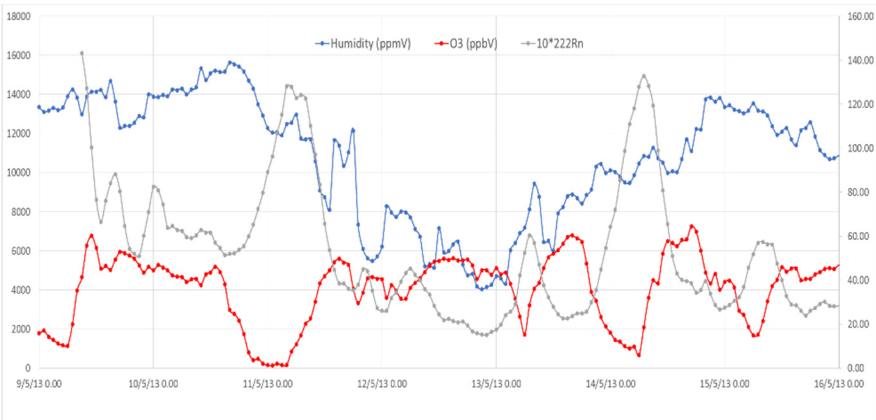

Figure 7: 9–16.05.2013. Plot of humidity (in ppmV, scale left), ^{222}Rn (in Bq m^{-3}, scale right) and ozone (in ppbV, scale right), from JRC-Ispra station, Italy.

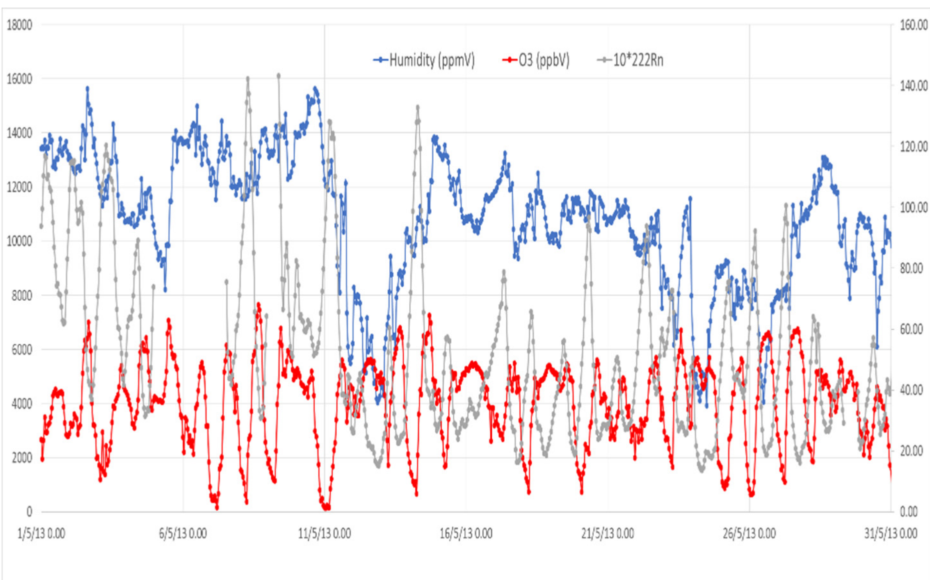

Figure 8: Plot of humidity (in ppmV, scale left), ^{222}Rn (in Bq m^{-3}, scale right) and ozone (in ppbV, scale right) for May 2013, from JRC-Ispra station, Italy.

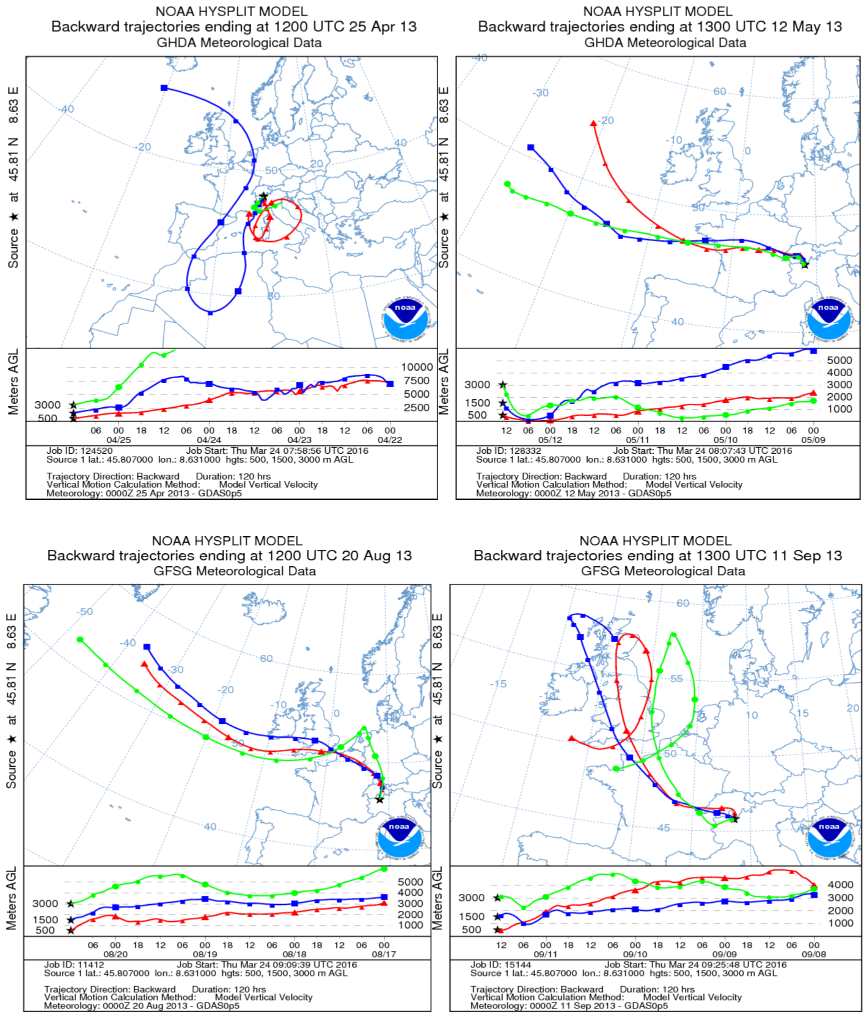

Figure 9: Examples of Hysplit trajectories year 2013 (*http://www.ready.noaa.gov/HYSPLIT_traj.php*).

4 CONCLUSIONS

Numerous entrainment episodes and Foehn episodes were observed at a measuring station in the North of Italy, during the time frame 2006–2015.

Daytime ozone showed a positive correlation to the ratio $^{7}Be/^{210}Pb$ for all years, but with large variations in the correlation coefficient between the years, indicating that the importance of transport of ozone from stratosphere/upper-troposphere have large variations from year-to-year.

In this investigation $^{7}Be/^{210}Pb$ had a mono-modal log-normal distribution. Lee et al. [20] found a bi-modal log-normal distribution at two high-altitude sites, where the second mode was attributed to episodes of stratospheric-intrusions. Thus, it appears that we do not see, at the low altitude JRC-Ispra station, such clear-cut episodes dominated by stratospheric-intrusions, but a combination of ozone from *in situ* boundary layer photochemistry, tropospheric transport and stratospheric contributions. This conclusion is confirmed by looking at variations of the parameters O_3, humidity and ^{222}Rn, combined with back-trajectories.

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