AEROSOL SIZE SPECTRUM ANALYSIS AS SUPPORT TO DIFFERENTIATE LONG-RANGE MASS TRANSPORT AND ACUTE LOCAL POLLUTION EPISODES OF PARTICULATE MATTER

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ABSTRACT

Long-range transport of polluted air masses can significantly affects surface PM10 levels. PM10 daily-average ponderal values are inadequate to investigate the occurrence of such phenomena and consequently do not give significant information for source apportionment. In this work the analysis of aerosol size spectra and the study of the correlation of the fine and coarse modes of PM have been applied to individuate long-range transport episodes of polluted air masses. Dust-models and backward-trajectory analysis were supportive to local surface measurements of size distribution of PM in confirming the origins of remote sources of pollution. An application is discussed involving long range transport over Italy of desert dust, comparatively examined with a fine-PM pollution episode due to local sources.

Keywords: *Long-range transport, aerosol size spectra, coarse and fine mode correlation, natural radioactivity.*

1. INTRODUCTION

European standards for particulate matter (PM) monitoring rely on daily and annual limit values for PM10 that from 2010 should not exceed 20 μg m^{-3}, as annual level, with no more than seven days of exceedance of the daily limit value of 50 μg m^{-3}. Such limits, that apply to the whole European Union (EU), do not consider the geographic and meteorological peculiarity of the different regions within the EU. Surface levels of particulate matter (PM) concentration have been widely reported to be affected by the long range transport of polluted air masses. Southern European regions, in particular the Mediterranean basin, are influenced by the dust transported from North Africa (Sahara and Sahel deserts) (CAFE Working Group on Particulate Matter, 2004). This source is far less significant in the Northern latitudes owing to the greater distances and to the different meteorology of these areas. According to the Directive 1999/30/EC, when the limit values for PM10 are exceeded as a consequence of natural events which result in concentrations significantly in excess of normal background levels from natural source, Member States shall provide the necessary justification for that. They are obliged to implement action plans (Directive 96/62/EC) only when the limit values are exceeded due to causes other than natural events.

In this context, it is important to recognize the occurrence of such events. To that purpose, PM10 daily-average ponderal values are inadequate to investigate such fine/coarse pollution episodes and consequently do not give significant information on its source apportionment. More information can be obtained studying the size distribution of atmospheric PM and the temporal evolution of the correlation between the coarse and the fine modes. With this aim, such approach has been applied in this study and two pollution episodes have been comparatively examined, the first occurred on March 2007 and linked to local sources, the second due to long range dust transport on August 2007.

2. MATERIALS AND METHODS

The approach adopted relies on the analysis of the aerosol aerodynamic-diameter spectra to highlight the contribution of long-range transport of polluted air masses. To this purpose, the temporal evolution of the correlation of the coarse and of the fine fractions was studied. Dust-models and backward-trajectory analysis were supportive to local surface measurements of size distribution of PM in confirming the origins of remote sources of pollution.

The study was carried out in Montelibretti, a rural area in the northern periphery of Rome, where daily-average PM10 and PM2.5 were measured and aerosol size-spectra were continuously taken.

PM10 and PM2.5 levels were measured using a FAI SWAM 5a Dual Channel Monitor. The instrument is an automatic sampling and mass measurement system, working with two independent sampling lines. The PM samples are accumulated on filtering membranes and their mass is determined by the β-attenuation technique.

Aerodynamic size distributions of atmospheric aerosol were measured by means of a TSI Aerodynamic Particle Sizer 3321 (APS). The APS spectrometer measures the time of flight of single particles, when they are accelerated through a nozzle, using two overlapping laser beams (Wilson et al., 1980; Dahneke, 1973). Particles are counted and sized, in the range from 0.5 to 20 μm (aerodynamic diameters), in fifty size channels. 5-minutes averaged size distributions were continuously taken in Montelibretti (Rome). Particle mass concentrations have been calculated from number concentration by APS software, assuming 2 g cm^{-3} average particle density (TSI application note). The 0.58 μm and 3.52 μm APS size channels have been considered as representative of the coarse and of the fine fractions to study the correlation between the two modes. At each hour of the day, with 5-minute time resolution, the Pearson's coefficient of correlation has been calculated, considering the data-points referring to the subsequent 24 hours. Such time-span has been considered since the phenomena investigated are on the time scale of some days.

Natural radioactivity was assessed, as a tracer of Planetary Boundary Layer (PBL) evolution (Perrino et al., 2001), using a FAI PBL Mixing Monitor. The instrument samples atmospheric PM on 47-mm membrane filters and by means of a Geiger detector, measures on it β-radioactivity of short-lived decay products of Radon.

Particulate nitrate in PM 2.5 samples has been measured by means of a Rupprecht & Patashnick 8400 Ambient Particulate Nitrate Monitor. The instrument consists of a pulse generator, where sample conditioning, collection and flash vaporization on a NiChrome strip takes place, and a NOx Pulse Analyzer, where nitrogen oxides evolved from flash vaporization and nitrate reduction are quantified.

The interpretation of the aerosol size spectra was supported by dust-models and backward-trajectory analysis to assess the origin of the long-range transported air masses. Dust simulations were performed by the Navy Aerosol Analysis and Prediction System (NAAPS) predicting the distribution of tropospheric aerosols. The model, developed by the Naval Research Laboratory (NRL) in Monterey - CA (http://www.nrlmry.navy.mil/aerosol/), is a modified form of that developed by Christensen (Christensen, 1997). The NRL version uses global meteorological fields from the Navy Operational Global Atmospheric Prediction System (NOGAPS), analyses and forecasts on a 1 X 1 degree grid, at 6-hour intervals and 24 vertical levels reaching 100 mb.

Backward-trajectories were calculated by means of the HYbrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT), available at the NOAA Air Resources Laboratory (ARL) (http://www.arl.noaa.gov/ready/hysplit4.html).

3. RESULTS AND DISCUSSION

The local PM pollution episode on March 2007

The PM pollution episode observed in Montelibretti (center-Italy) in the period from March 10th to March 21st 2007 was also observed in Milan (north-Italy) as shown respectively in figures 1-a and 1-b, reporting PM10 and PM 2.5 data. The evolution of the PM2.5 trends that passed from 12.3 μg m^{-3} (March 10th) to 42.2 μg m^{-3} (March 17th) and from 16.0 μg m^{-3} (March 10th) to 64.1 μg m^{-3} (March 16th), respectively in Montelibretti and in Milan, suggests that the high PM10 values measured in the period investigated were mainly due to the contribution of the fine fraction.

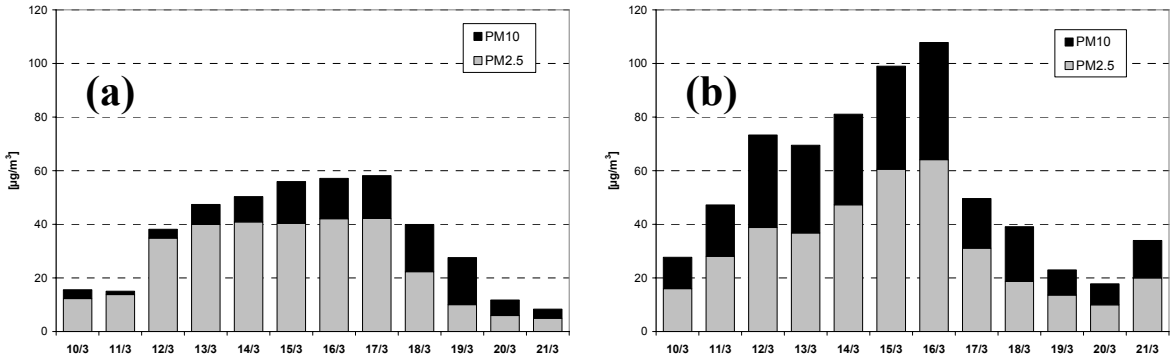

Figure 1: Daily-average PM10, PM2.5 values measured in Montelibretti (a) and Milan (b) in the period March 10th – 21st

Accordingly with the PM2.5 patterns, aerosol size spectra (Figure 2) in Montelibretti clearly show a substantial increment of the fine fraction, that on March 17th at 08:00 reached values about 15 times higher than those measured on March 10th at 00:00.

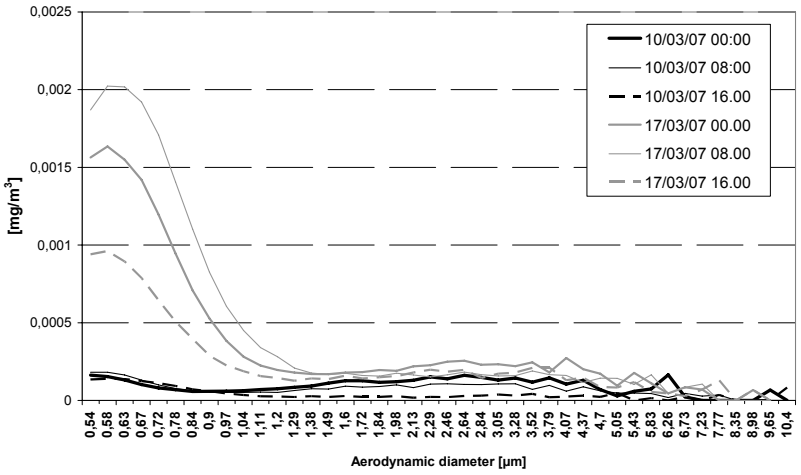

Figure 2: Aerosol size spectra measured at different hours on March 10th and 17th, 2007 in Montelibretti (Rome)

The trend of variation of the fine fraction closely followed that of natural radioactivity as shown in figures 3 a-b, where the daily trends of the 0.58 (representative of the fine mode) and 4.06 μm APS size channel are reported together with the natural radioactivity. Such occurrence suggests that the high levels of PM2.5 were attributable to the presence of high pressure stable atmospheric conditions, presumable over a mesoscale area, given the same trend of PM10 and PM2.5 observed in Montelibretti and Milan (Figures 1 a-b), that favoured the pollutant accumulation. On the contrary, the periods from March 10th to 11th and from

March 19th to 21st were characterized by very low levels of natural radioactivity, very likely due to advective conditions that coherently favoured pollutant dispersion, as shown by the low levels of the fine fraction (0.58 µm size channel in figure 3-a).

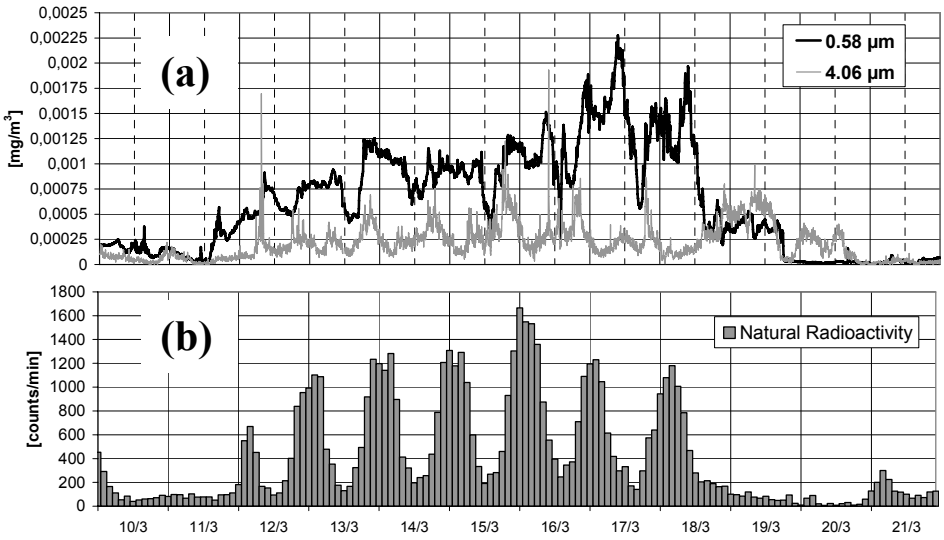

Figure 3: Daily trends of the 0.58 and 4.06 µm APS size fractions (a) and of natural radioactivity (b) in Montelibretti (Rome) in the period March 10th-21st

Accordingly, the pattern of a secondary pollutant such as particulate nitrate (Figure 4) followed very well that of the 0.58 µm APS size channel, with an increasing trend when the atmospheric conditions favoured the pollutant stagnation and the formation of secondary PM.

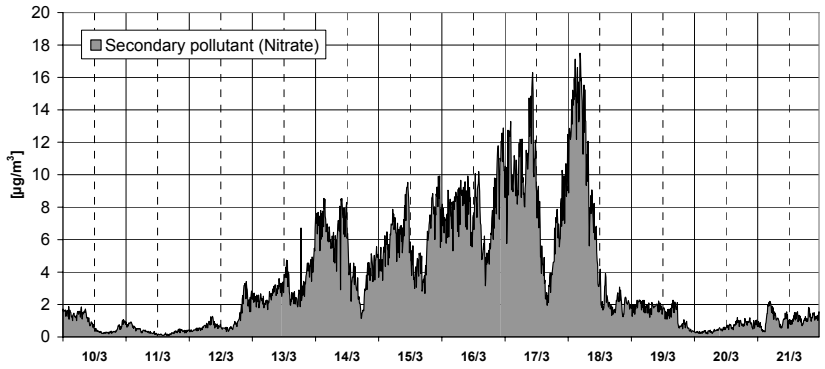

Figure 4: Daily trend of particulate nitrate in Rome in the period March 10th-21st, 2007

That the episode of March 2007 was due to local sources of pollutions, amplified by stable atmospheric conditions, is further demonstrated by the very low wind velocity (Figure 5) measured in the period from March 13rd to 18th, in comparison with those registered during the periods of low natural radioactivity, from March 10th to 11th and from March 19th to 21th.

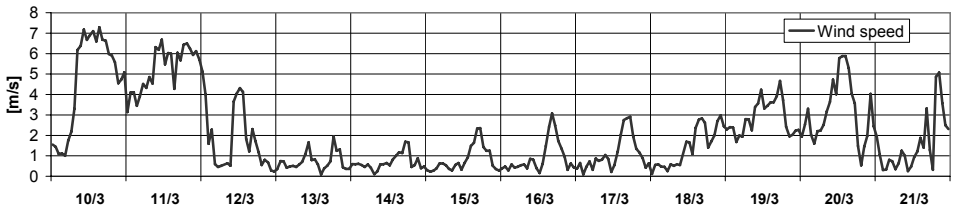

Figure 5: Daily trend of the wind velocity in Montelibretti (Rome) in the period March 10th-21st, 2007

The long-range transport episode on August 2007

When atmospheric pollution is dominated by local sources PM10 daily average values as high as 40 μg m^{-3} are peculiarly expected on August in Rome. The PM10 levels measured in the period, investigated significantly higher than the expected values, were strongly suggestive of the occurrence of long-range air mass transport of PM. The trend of daily average values of PM10 was characterized by peak values of 54, 38 and 72 μg m^{-3} respectively on August 22nd, 25th and 30th (Figure 6). The same trend was followed by the coarse fraction (PM10-PM2.5), evidencing that such fraction was responsible of the high PM10 values measured.

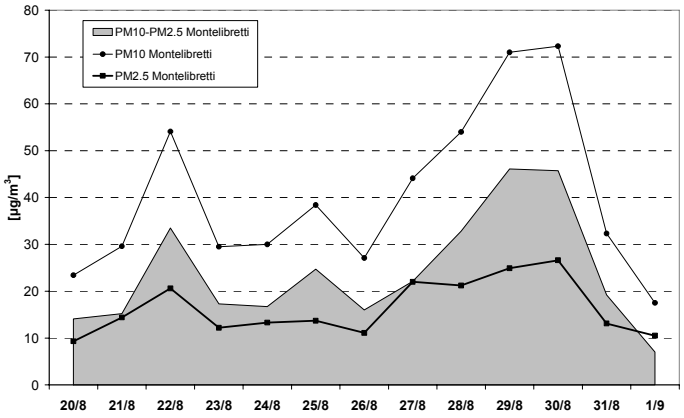

Figure 6: Daily-average PM10, PM2.5 and PM10-PM2.5 values measured in Montelibretti (Rome) in the period August 20th – September 01st, 2007

To investigate the scale of the pollution episode, PM10 values in Rome (ARPA Lazio) were compared with those measured in south Italy in Brindisi (ARPA Puglia) and in north-Italy in Verona (ARPA Veneto) (Figure 7). PM10 levels measured in Brindisi and in Rome shared the same trend of variation with three peaks values, while in the PM10 pattern observed in Verona the first peak (on August 22nd) was lacking. Figure 8 describes the APS aerosol size spectra measured in Montelibretti (Rome) at 00:00 on August 20th and September 02nd, before and after the PM10 events (Figure 6) and on August 23rd, 26th and 31st, on the three PM10 peaks (Figure 6). Figure 8 shows significant increments of the coarse fraction, that, on August 23rd, 26th and 31st, were respectively about 2.5, 1.5 and 3.5 times higher than the values measured on August 20th. Figure 9-a shows the daily trend of 0.54, 0.58, 0.63 μm, (representative of the fine mode) and of 3.52, 3.79, and 4.07 μm (representative of the coarse mode) APS size channels together with the Pearson's coefficient of correlation of 0.58 μm and 3.52 μm APS size channels (Figure 9-b). The coarse and the fine fractions vary from being well correlated to totally lacking of correlation. Moreover in some periods the coefficient of correlation has negative values indicating that one fraction varies along a decreasing trend, while the other follows an increasing pattern of variation. Such behaviour can be understood observing the pattern of variation of the natural radioactivity (figure 9-d): when the radioactivity suddenly dropped, denoting higher degree of dilution of atmospheric pollutants, the fine fraction of PM (represented through the 0.54, 0.58 and 0.63 μm APS size channels) accordingly decreased, while, on the contrary, the coarse fraction (3.52, 3.79 and 4.07 μm APS size channels) increased.

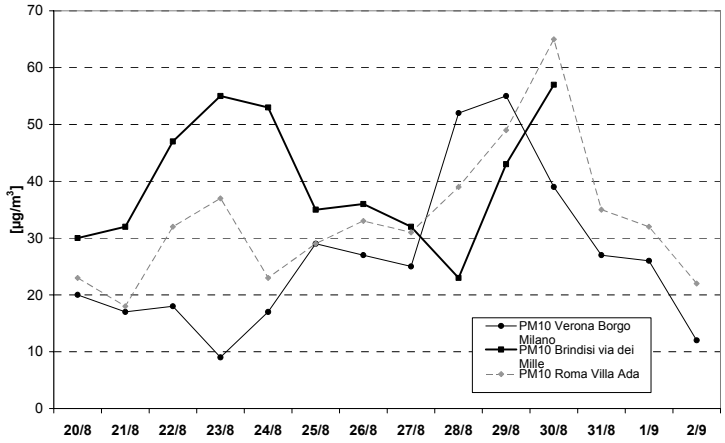

Figure 7: Daily-average PM10 values measured at ARPA monitoring stations in Brindisi, Rome and Verona in the period August 20th – September 02nd, 2007

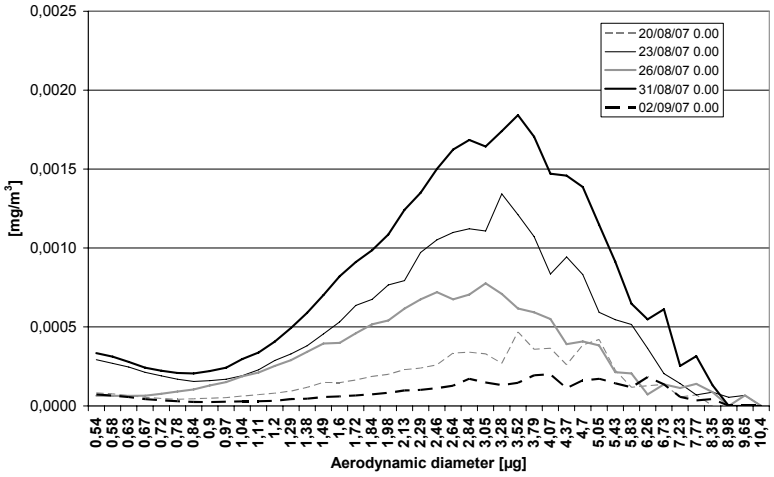

Figure 8: Aerosol size spectra measured at 00:00 on August 20th, 23rd, 26th 31st and September 02nd, 2007 in Montelibretti (Rome)

Such apparent contradiction (i.e. the degree of dilution of the low atmosphere increases and the fine PM concentration increases too), is explained admitting a remote source of fine PM, very likely transported through the inflow of new air masses. When radioactivity dropped, due to the increased vertical degree of mixing, the coarse PM surface concentration increased, instead of decreasing, as a consequence of an increased vertical transport with dust rich streams sinking from the higher atmospheric layers.

The origin of such dust is indicated by the NAAPS maps of dust surface concentrations (Figures 10 a-c) and by the HYSPLYT 96-hours backward trajectories to Brindisi (south-Italy), Rome (center-Italy) and Verona (north-Italy) at 1500 m height (Figures 10 d-f) that, accordingly with the PM10 patterns recorded in these cities (Figure 7), show no dust transport on August 21st. Advection of Saharan dust occurred on August 22nd, reaching Brindisi and Rome but not Verona, where, on such day, relatively low PM10 levels were measured (Figure 7). On August 25th and 30th the inflow of desert dust involved the whole Italian peninsula (Figure 10-c, f).

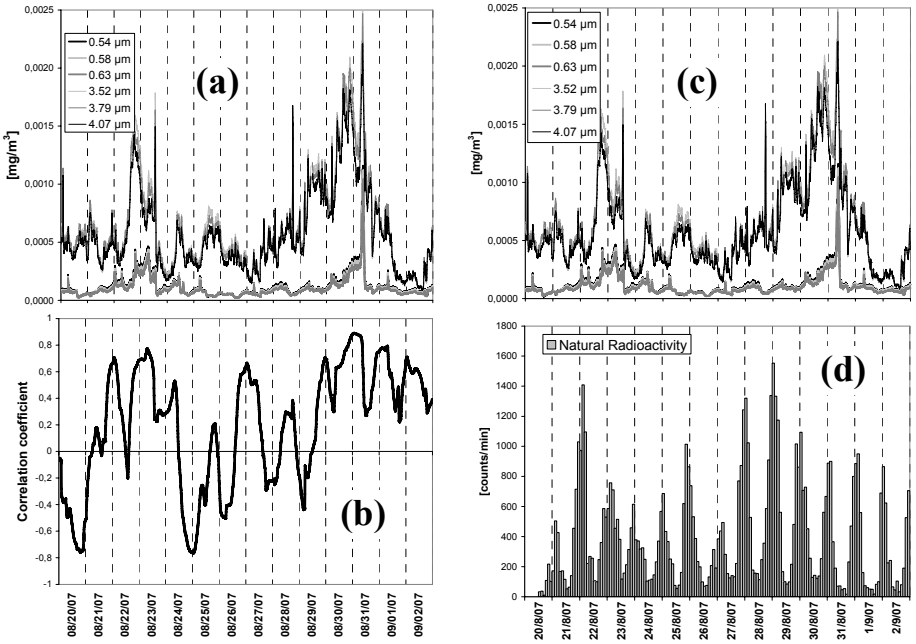

Figure 9 a), c) Daily trends of the 0.54, 0.58, 0.63, 3.52, 3.79, and 4.07 µm APS size fractions in Montelibretti (Rome). b) Pearson's coefficient of correlation of 0.58 µm and 3.52 µm APS size-fractions, from August 20th to September 02nd d) Daily trend of natural radioactivity, in the period August 20th – September 02nd, in Montelibretti

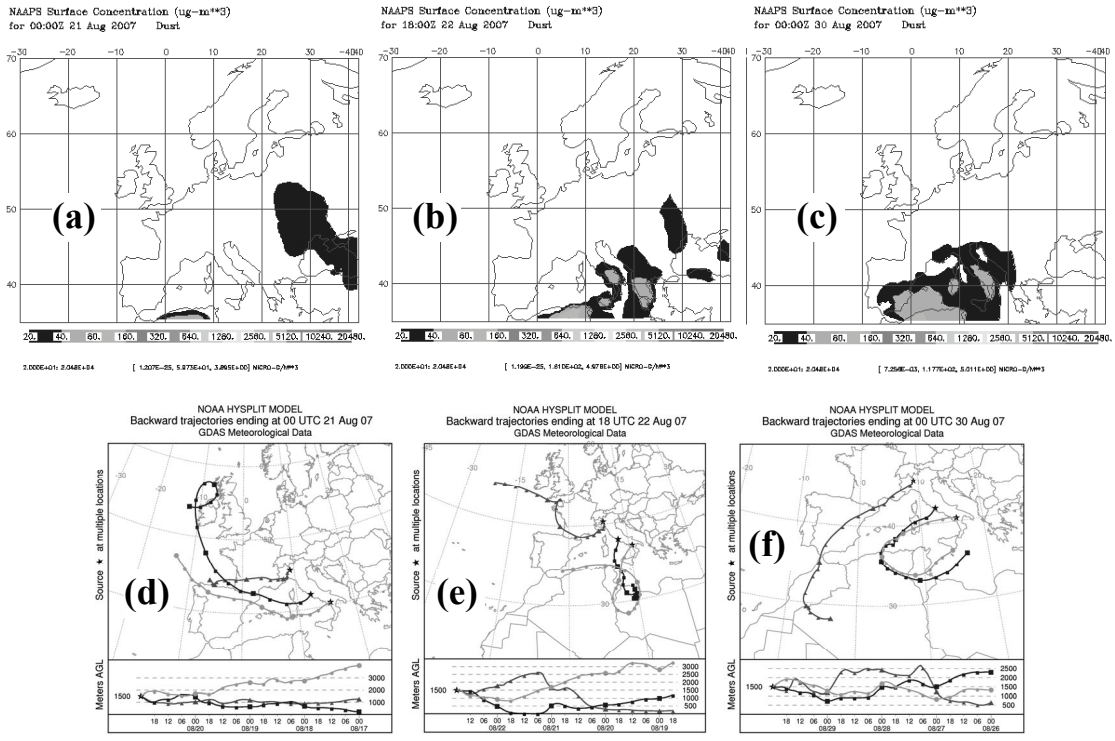

Figure 10: NAAPS "Dust" plot at surface level on August 21st at 00 UTC (a), August 22nd at 18 UTC (b), August 30th at 00 UTC (c). HYSPLIT 96 h backward air mass trajectories to Verona, Rome, Brindisi at 1500 m above ground level, on August 21st at 00 UTC (d), August 22nd at 18 UTC (e), August 30th at 00 UTC (f)

4. CONCLUSIONS

Atmospheric stability and low wind velocities, as revealed by well structured and high levels of natural radioactivity are conditions favouring pollutant stagnation and the formation of fine secondary PM. Acute pollution episode determined by local sources can then be recognized in such situations, observing how the PM concentration pattern follows the evolution of natural radioactivity.

Dust from desert areas is transported at high altitudes and then produces high coarse PM surface concentrations in conditions of high vertical degree of atmospheric remixing, that otherwise would favour pollutant dilution. As result of that, when natural radioactivity drops (high degree of remixing) the coarse mode concentration increases, while the fine fraction concentration decreases. The two mode then appear anticorrelated (negative values of Pearson's coefficient of correlation).

The results obtained draw the attention to the importance of highly time-resolved measurements in understanding the origin of atmospheric PM. The frequency of measurement should be comparable with the time scale of the evolution of atmospheric PBL.

5. ACKNOWLEDGEMENTS

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