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POLLUTED DAYS AND CLEAN DAYS: DIFFERENCES IN THE DILUTION POTENTIAL OF THE LOWER ATMOSPHERE AND IN THE MASS CONCENTRATION AND CHEMICAL COMPOSITION OF ATMOSPHERIC PARTICLES

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ABSTRACT

The mass concentration and chemical composition of PM_{10} and $PM_{2.5}$ has been determined daily during several field campaigns carried out in Central Italy. The studies were addressed to elucidate which chemical components were mainly responsible for the increase of particle concentration during pollution episodes.
During the studies, the dilution properties of the lower atmosphere have been estimated on the basis of natural radioactivity measurements. The results confirm that the atmospheric mixing plays a primary role in determining anthropogenic pollution episodes and indicate that during stability periods the increase in PM concentration is mainly due to carbon compounds and ammonium salts.

Key words: Atmospheric pollution, Particulate matter, Natural radioactivity, Atmospheric stability, Ammonium nitrate

1. INTRODUCTION

The limit values for PM_{10} concentration, set in the European Union by the First Daughter Directive to the Air Quality Framework Directive, address both annual average concentration (40 ug/m^3) and daily average concentration (50 ug/m^3, to be exceeded no more than 35 times a year). In this perspective, the understanding of the different mechanisms that stay behind the increase in particle air concentration has become particularly important.
The comprehension of a pollution event requires not only the accurate determination of the chemical composition of the atmospheric particles but also the elucidation of the role played by the dilution properties of the lower atmosphere. The increase in the air concentration of a pollutant, in fact, is the result of the combination of the emission (and/or production) of the pollutants in the atmosphere and of the reduced capacity of the atmosphere to dilute them.
Information about the mixing properties of the boundary layer can be easily obtained by monitoring natural radioactivity due to Radon short-lived decay products. The emission flow of Radon from the ground, in fact, can be considered to be constant in the time and space scale of our observations; it follows that Radon air concentration at a given location only depends on the dilution factor. By determining the natural

radioactivity due to the Radon progeny attached to atmospheric particles we can obtain a reliable picture of the dilution properties of the lower atmosphere (Perrino et al., 2001, Vecchi et al., 2004).
The study of the mixing properties of the lower atmosphere allows us to identify periods characterised by a weak atmospheric mixing, which favour the occurrence of anthropogenic primary and secondary pollution events, as well as periods characterised by advection, during which natural pollution events may be recorded. The subsequent chemical analysis of the atmospheric particles allows a complete characterisation of the pollution event. The complex chemical nature of particulate matter prevents the determination of all the chemical species, but the bulk determination of the main compounds (elemental carbon, inorganic compounds – main ions and metals - and organic carbon as a total value) is sufficient to identify the natural or anthropogenic characteristics of each pollution episode, and to estimate the primary and secondary contribution to anthropogenic events (Chan et al., 1997, Marcazzan et al., 2001, Harrison et al., 2003, Harrison et al., 2004, Rees at al., 2004, Hueglin et al., 2005).

2. EXPERIMENTAL

The data reported in this paper have been collected during two field studies. The first one was carried out during the summer and the winter of 2003 in the framework of a research project funded by the Municipality of Rome and addressed to obtain a first characterisation of the chemical nature of particulate matter in the Rome area. The determinations were carried out at the urban background station of Villa Ada (VA), sited inside a park in the urban area of Rome, at a traffic station in Rome and at the semi-rural station of Montelibretti (ML) sited about 30 km NE of the centre of the city.
The second field study was carried in the framework of the Project “Fine Particles”, funded by the Lazio Region and aimed to characterise PM_{10} and $PM_{2.5}$ pollution events in the area of the Region. It was carried out between October 2004 and July 2005 in six sampling stations, the VA station and a traffic station in Rome, the ML station, two urban stations in the cities of Viterbo and Latina and the regional background station of Fontechiari.
During both studies, natural radioactivity was measured by means of a automated stability monitor (PBL Mixing Monitor, FAI Instruments, Fontenuova, RM-I) that basically consists of a particulate matter sampler equipped with a Geiger–Muller counter for determining the total beta activity of the short-lived radon progeny. The instrument is automatic and operates on two filters at the same time: sampling is performed on the first filter for a 1-h sampling duration, then this filter undergoes the beta measurement phase while a second filter undergoes the sampling phase (residual radioactivity is taken into account by a software procedure). These instrumental features assure that the short-lived beta activity of the particles is determined continuously over an integration time of 1 h with a beta measurement period long enough to guarantee a good accuracy of the results.
Particulate matter concentration was determined on a daily basis by means of two beta monitors: SWAM5a (FAI Instruments, Fontenuova, RM-I) or SM200 (Opsis

AB, Furulund-S).
During the 2003 study EC/OC compounds were determined, over 6-h time periods, by means of a automatic monitor employing a direct-measuring thermal-CO_2 technique (Series 5400 Ambient Carbon Particulate Monitor, Rupprecht & Patashnick Co, NY-USA). During the 2004-2005 study, the EC/OC compounds were daily collected on quartz filters and then analysed by means of a thermo-optical analyser (OCEC Carbon Aerosol Analyser, Sunset Laboratory, OR-U.S.A.).
For the analysis of ions and metal content, particulate matter was daily collected on Teflon filters. These were analysed for their metal content (Al, Si, Fe, Mg, Ca, Ti, S) by energy-dispersion X-ray fluorescence (X-Lab 2000, Spectro Italia, MI-I), then extracted in a water solution and analysed for their anionic (Cl^-, NO_3^-, $SO_4^{=}$) and cationic (Na^+, $NH4^+$, K^+, Mg^{++} Ca^{++}) content by ion chromatography (IC, DX100, Dionex Corporation, CA-U.S.A.).

3. RESULTS AND DISCUSSION

Anthropogenic events

The time pattern of natural radioactivity measured at the urban background station of Rome during the campaigns of summer and winter 2003 is reported in Figure 1. The difference between the two graphs reflects the difference in the mixing properties of the lower atmosphere between warm and cold months: during the summer atmospheric stability during the night (high values of natural radioactivity) regularly alternates to convective mixing during the day (low values of natural radioactivity). During the winter, instead, advection periods, with constantly low values of natural radioactivity (December 7-9, 16 and 22-25) alternate to stability periods, with low mixing of the atmosphere during the night but also during the day (December 6, 14, 17-21).

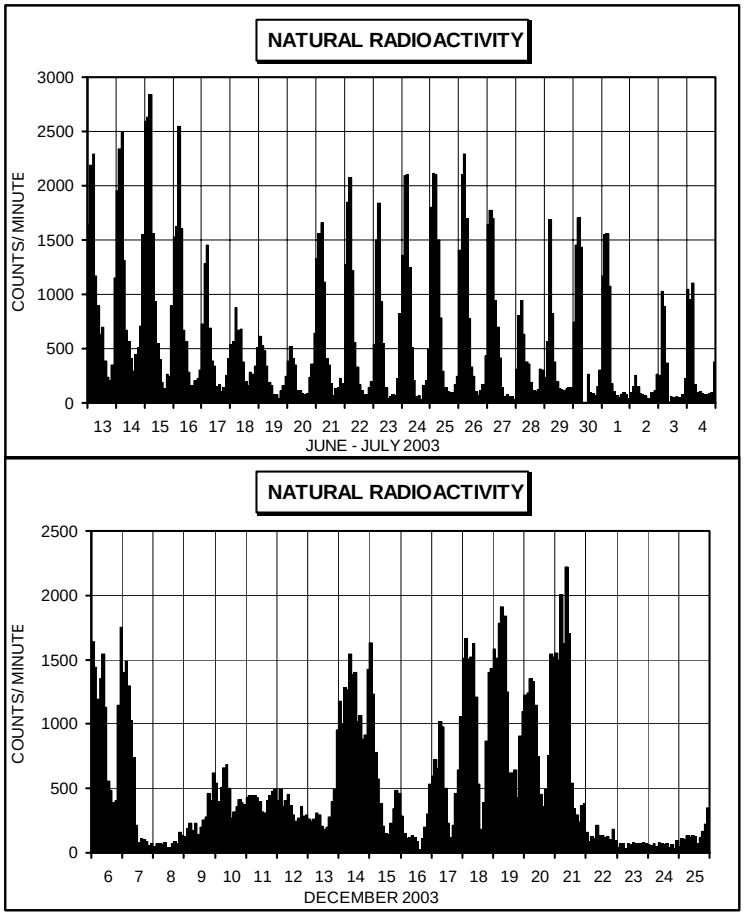

Figure 1: Time pattern of natural radioactivity during the summer (upper) and the winter (lower) campaign in Rome.

These differences in the

dilution properties of the lower boundary layer result in a different modulation of the particle concentration: although the average concentration of PM_{10} during the two periods were quite similar (33.9 ug/m^3 during the summer campaign and 38.3 ug/m^3 during the winter campaign at the urban background station, 28.5 and 30.8 ug/m^3, respectively, at the rural station), the relative standard deviations are very different: around 20% for the summer period and more than 50% for the winter period. Considering the whole year 2003, about 70% of the exceedances of the limit value of 50 ug/m^3 at the urban background station were recorded during the winter period.
The time patterns of PM_{10} and $PM_{2.5}$ at the VA and ML stations during the two field studies, reported in the left side of Figure 2, show that the concentration at the two sites were very similar. This finding indicates that the particulate concentration measured at the urban background station can be mostly attributed to regional-scale pollution. At the traffic station (right-hand side of Figure 2), during the summer campaign the level of PM_{10} was very close to the VA and ML levels, while during the winter campaign we can distinctly observe higher values at the traffic station during the atmospheric stability periods, mainly during the multi-day period of December 17-21.

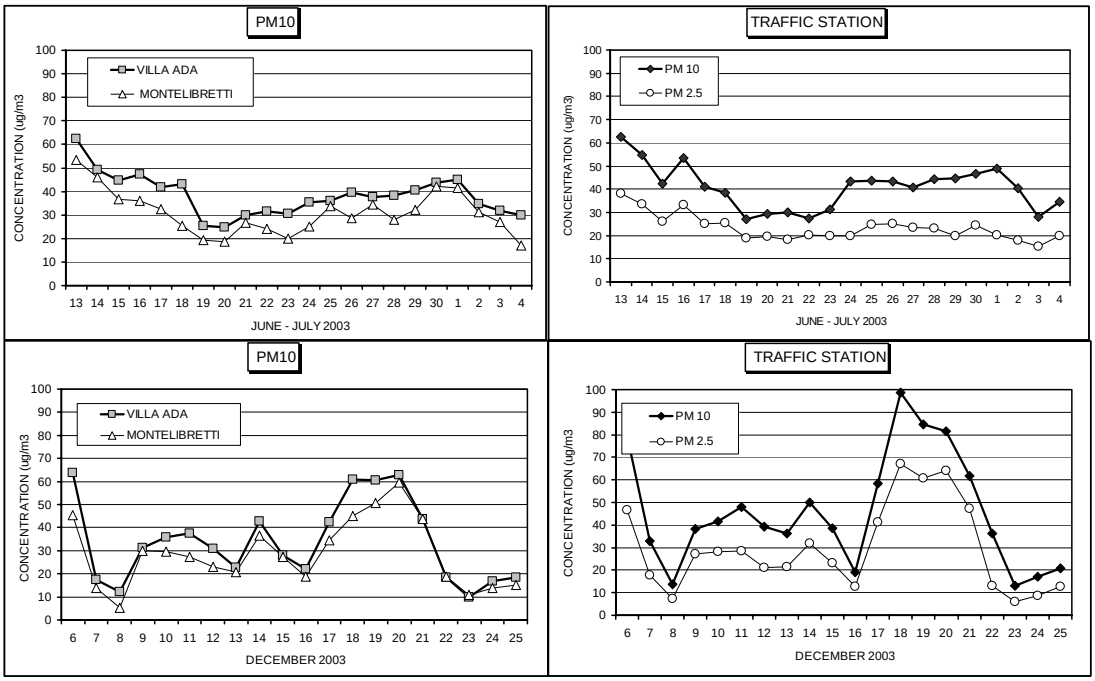

Figure 2 Left side: time pattern of PM_{10} concentration at the urban background station of Villa Ada (VA) and at the rural station of Montelibretti (ML).
Right side: time pattern of PM_{10} and $PM_{2.5}$ at a traffic station in the urban area of Rome.
Upper graphs refer to the summer campaign, lower graphs to the winter campaign.

The analysis of the chemical composition of atmospheric particles highlights that the increase of carbon compounds concentration is one of the main reasons for the increase of particle concentration during atmospheric stability periods. The graphs of Figure 3 show the comparison between the total concentration of carbon compounds and PM_{10} (left graph) and the time pattern of elemental carbon and organic carbon (right graph) at the urban background station during the winter campaign. In these

conditions, the main increment in carbon concentration is clearly due to organic compounds.

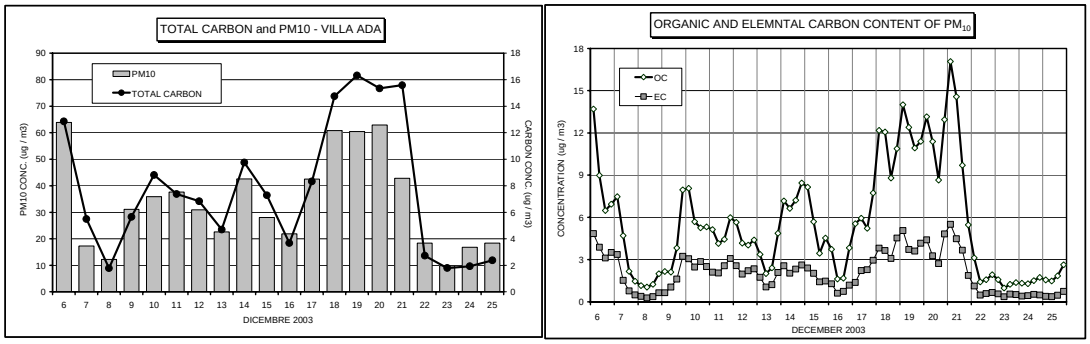

Figure 3: Comparison between PM_{10} and total carbon compounds (left graph) and between organic carbon and elemental carbon (right graph) at the urban background station during the winter campaign.

By comparing elemental carbon and organic carbon concentration at the urban background station with the values obtained at the traffic station (Figure 4) we can observe that elemental carbon concentration at the traffic station is much higher that at the urban background station, showing the influence of the vicinity of the emission sources (mainly Diesel vehicles). Organic carbon concentration, instead, is more dependent on the aging of the air masses (relevance of the secondary organic compounds) and the values at the two stations are quite similar.

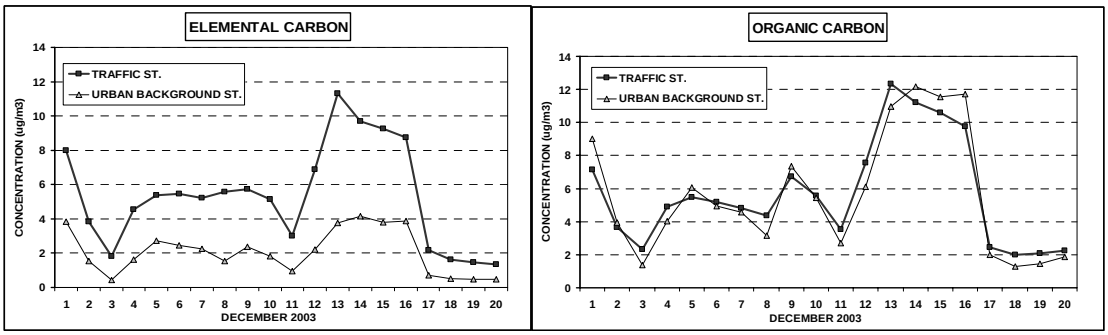

Figure 4: Comparison between elemental carbon (left graph) and organic carbon (right graph) at the traffic station and the urban background station during the winter campaign.

The other compound that can be considered as one of the main responsible for the increase of particulate matter concentration during atmospheric stability periods is ammonium nitrate. The increase of ammonium nitrate concentration at the background station and especially at the traffic station during the period 17-21 is evident from the data of Figure 5.

It should be stressed that when the collection of particles is carried out on a single filter membrane, as it is in most air quality network, the concentration of ammonium nitrate is generally underestimated, because of the negative bias due to the lost of the volatile fraction of ammonium salts during the sampling phase, the measurement phase and also during the period between the sampling and the chemical analysis (Rees et al., 2004).

An accurate determination of ammonium nitrate can be obtained only by using a filter pack composed of a Teflon filter followed by a Nylon (or an alkaline – impregnated) filter and an acid - impregnated filter for the recovery of nitric acid and ammonia evolved from ammonium nitrate salts. Two denuders must be placed upstream of the filter pack in order to remove, respectively, atmospheric nitric acid and ammonia.

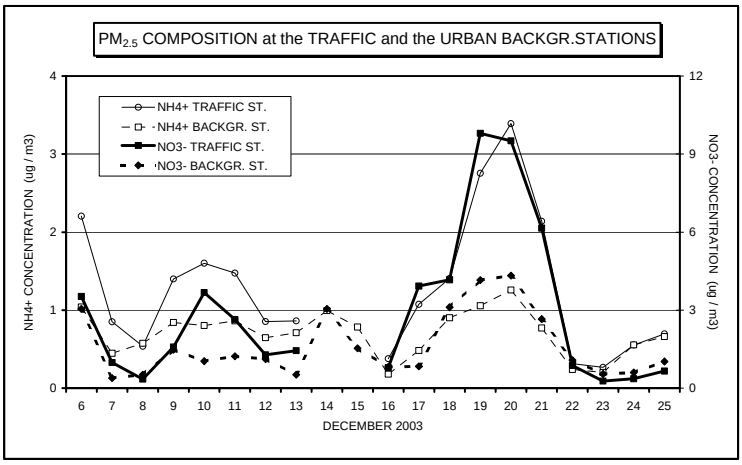

Figure 5: Ammonium and nitrate time pattern at the traffic and the urban background station during the winter campaign.

A field experiment was carried out during April 2005, aimed to investigate the influence of the internal temperature of the dust monitors on the recovery of ammonium nitrate. $PM_{2.5}$ was sampled at the Montelibretti station by means of the diffusion denuder / filter pack lines and by means of two co-located beta attenuation dust monitors. In the first instrument (SM200) the filter is heated at the temperature of 45°C during and after the measurement, until it is removed from the monitor. In the second instrument (SWAM5A), instead, the filter is kept at the local ambient temperature of 20°C. The results of the experiments, reported in Figure 6, show that in the case of a stable compound such as sulphate, the two monitors yield the same results, which are very close to the results yielded by the diffusion lines. In the case of nitrate, instead, less than 15% of the collected nitrate is, on average, lost by the 20°C monitor, and about 80% is, on average, lost by the

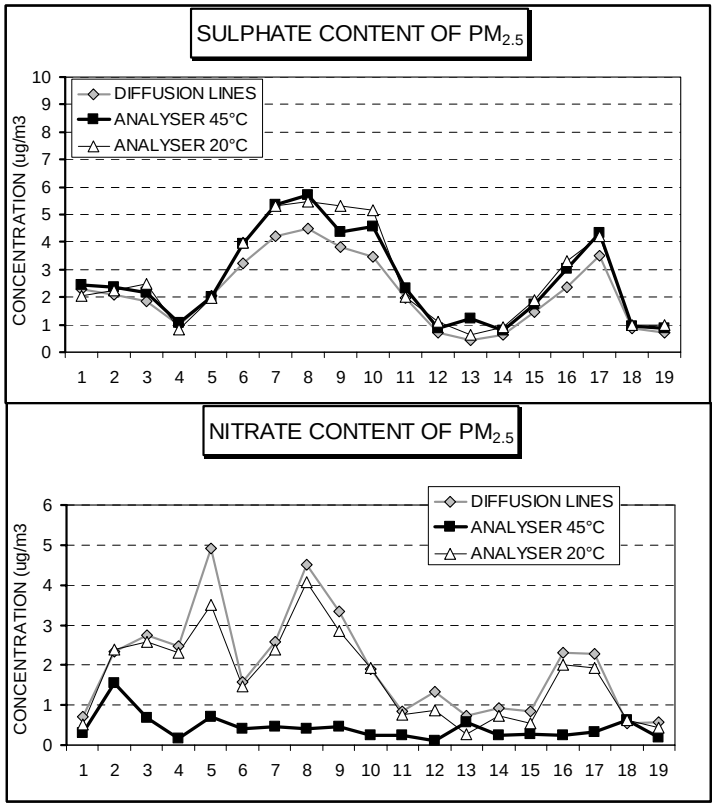

Figure 6: Comparison of sulphate and nitrate ion determined by denuder / filter pack diffusion lines and by heated and non-heated automatic monitors.

45°C monitor. These results indicate that the contribution of ammonium nitrate to PM concentration can be underestimated when a single filter is used, and that this underestimation may become severe in those automatic monitors where the filter membrane is heated.

Natural events

While anthropogenic pollution events are linked to a weak mixing of the lower atmospheric layers, natural events generally occur during advection periods, when the air masses may transport particles of natural origin from areas that can be also very far from the sites where the pollution events is recorded. In the area of Central Italy, two main types of natural events are frequently recorded: sea-spray transport from the Tyrrenian coasts and long-range transport of sand dust from North-African deserts. The occurrence of a natural event can be detected by the observation of low values of the natural radioactivity, which indicate advection, associated to an increase of the ratio between coarse and fine particles.

To detect the origin of a natural event and, in general, to obtain a reliable identification of the main sources of all particulate pollution events, it is important to carry out the analysis of the main components of atmospheric particles, that is ions, metals and EC/OC compounds.

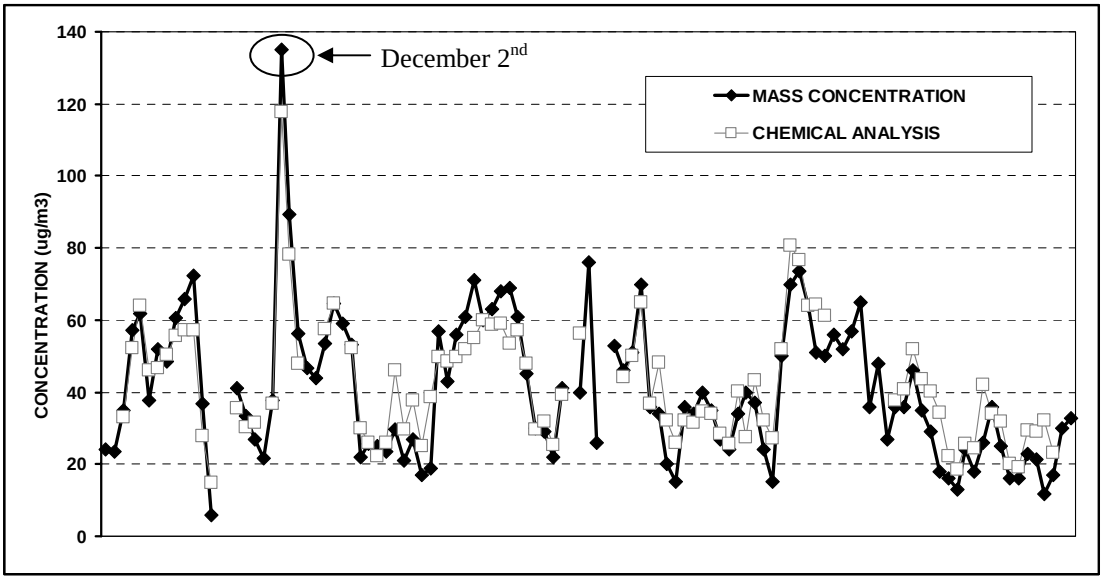

Figure 7: Comparison of the mass concentration of PM_{10} in Latina as measured by the Air Quality Network and as reconstructed by the chemical analysis.

An example of the comparison between the mass concentration of PM_{10} as measured by the local Air Quality Network and the sum of the chemical determinations carried out on the collected particles is reported in Figure 7. The data refer to the urban area of Latina, sited on the coast in the south of the Lazio region, and to 110 daily determinations carried out during the period October 2004 – April 2005. We carried out the reconstruction of the mass concentration from the chemical analysis by adding the contribution of anions (chloride, nitrate, sulphate), cations (ammonium, sodium, magnesium), metals (main components: aluminium, silicon, iron, calcium,

potassium), elemental carbon and organic carbon (without chemical speciation). Carbonate was calculated from the calcium and magnesium content; metal oxides were estimated as in Chan et al. (1997); the mass of organic material was calculated from the mass of organic carbon by multiplying OC by a factor ranging between 1.6 for urban traffic stations and 2.1 for rural station (Turpi and Lim, 2001; Rees at al., 2004). The very good agreement between the two data sets (R^2= 0.861) indicates that the quantitative analyses of the main components of the particulate samples give really reliable results.

The analysis of the crustal matter and of the sea spray aerosol for the six station participating in the "Fine Particles" project showed that both these type of events are common in Central Italy (Figure 8) and that during these events the natural components may reach up to 50% of the PM_{10} mass concentration.

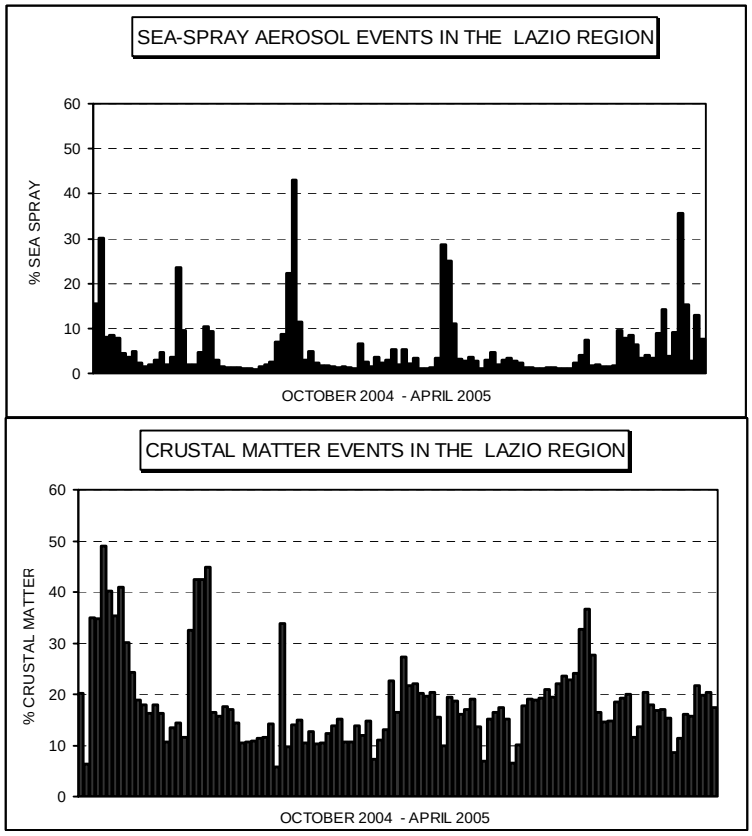

Figure 8: Per cent contribution of sea-spray and of crustal components to PM_{10} concentration in the Lazio region.

However, sea-spray aerosol is generally a minor constituent of PM_{10} (1-3%) and even during the transport of air masses from the sea the increase in PM_{10} mass concentration due to these compounds does not generally exceed 10 ug/m^3. It follows that sea-spray events are generally "clean" events, with PM_{10} concentration below the limit values.

Crustal components, instead, generally constitute 10-20% of the PM_{10} concentration, and during sand events the contribution of these species to PM_{10} may even exceed 100 ug/m^3. As a consequence, episodes of dust transport from the African desert, although not frequent, may easily cause exceedances of the limit values (in Figure 7, see the episode of December 2nd, when the PM_{10} concentration in Latina was close to 140 ug/m^3).

4. CONCLUSIONS

The joined use of the natural radioactivity monitoring for the evaluation of the mixing properties of the lower boundary layer and of the chemical analysis of the main constituents of atmospheric particulate matter constitute a sound and reliable

tool for the study of particulate pollution events and for the identification of natural episodes and of anthropogenic primary and secondary episodes.

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REFERENCES

Chan, Y.C., Simpson, R.W., McTainsh G-H- and Vowles P.D., 1997. Characterisation of chemical species in $PM_{2.5}$ and PM_{10} aerosols in Brisbane, Australia. Atmos. Environ. 31, 3773-3785.
Harrison, R. M., Jones, A.M., Lawrence, R.G., 2003. A pragmatic mass closure model for airborne particulate matter at urban background and roadside sites. Atmos. Environ. 37, 4927-4933.
Harrison, R. M., Jones, A.M., Lawrence, R.G., 2004. Major components of PM_{10} and $PM_{2.5}$ from roadside and urban background sites. Atmos. Environ. 38, 4531-4538.
Hueglin, C., Gehrig, R., Baltensberger U., Gysel M., Monn C. and Vonmont H., 2005. Chemical characterisation of $PM_{2.5}$, PM_{10} and coarse particles at urban, near-city and rural sites in Switzerland. Atmos. Environ. 39, 637-651.
Marcazzan, G.M.,Vaccaro, S., Valli, G., Vecchi, R, 2001. Characterisation of PM_{10} and $PM_{2.5}$ particulate matter in the ambient air of Milan (Italy). Atmos. Environ. 35, 4639-4650.
Perrino, C., Pietrodangelo, A., Febo, A., 2001. An Atmospheric Stability Index based on Radon progeny measurements for the evaluation of primary urban pollution. Atmos. Environ. 35, 5235-5244.
Rees S.L., Robinson, A.L., Khlystov A., Stanier, C.O., Pandis, S.N., 2004. Mass balance closure and the Federal reference Method for $PM_{2.5}$ in Pittsburgh, Pennsylvania.). Atmos. Environ. 38, 3305 – 3318.
Turpin, B. and Lim, H., 2001. Species contribution to $PM_{2.5}$ mass concentration: revisiting common assumption for estimating organic mass. Aerosol Sci. and Technol. 35, 602-610.
Vecchi, R., Marcazzan, G, Valli, G., Cerini, M and Antoniazzi, C., 2004. The role of atmospheric dispersion in the seasonal variation of PM_1 and $PM_{2.5}$ concentration and composition in the urban area of Milan (Italy). Atmos. Environ. 38, 4437-4446.