

# ATMOSPHERIC PARTICULATE MATTER

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**Abstract:** Atmospheric aerosol constitute one of the most challenging issues in environmental research. The main physico-chemical characteristics, sources and effects of this pollutant are briefly reported in this paper, together with some experimental results regarding the strength of the main emission sources and formation pathways. The relevant role of the dilution properties of the atmosphere in driving the mass concentration of atmospheric particulate matter and in determining high pollution events is elucidated. Some episodes of biomass burning pollution and desert dust long-range transport are discussed.

## 1 PHYSICAL CHARACTERISTICS

Atmospheric particulate matter (PM) is generally defined as a mixture of solid and/or liquid particles that remains individually dispersed in the air. Atmospheric PM can be emitted by a wide variety of sources that influence its physical properties (size, surface area, density), chemical composition and size distribution. In particular, PM may be classified as primary or secondary in accordance with its formation mechanism: primary particles are directly emitted into the atmosphere while secondary particles are formed after chemical transformation of their gaseous precursors.

PM may vary in size from a few nanometers to several tenths of micrometers. Its typical size distribution, shown in Figure 1, includes three different modes, differing also in terms of generation process (John, 2001). The nucleation mode (or ultrafine particle mode) includes particles having equivalent diameter below 0.1  $\mu\text{m}$ , which are formed by the homogenous nucleation of precursor gases and from combustion processes. The accumulation mode includes particles in the range 0.1 -1  $\mu\text{m}$ , formed by coagulation of particles in the nucleation mode and by condensation of gaseous species on the surface of pre-existing particles. The coarse mode (over 1  $\mu\text{m}$ ) includes particles formed by mechanical processes, such as erosion of the earth surface (mineral dust) and of other materials, including the ocean surface (sea spray).

Ultrafine particles have the highest number density, while particles in the coarse mode are characterized by high mass density. Although the coarse mode is dominated by primary particles, also secondary particles formed by the chemical interaction of gases with primary particles of crustal or marine origin can be found in this mode.

Particles residence time in the atmosphere also depends on their size. Owing to the effect of gravity, coarse particles are rapidly removed from the air by sedimentation (residence time between some minutes and some hours); also, particles in the nucleation mode are rapidly transformed into coarser particles by coagulation processes. The highest residence time in the atmosphere (up to some weeks) is shown by particles in the accumulation mode, which can be easily transported by the wind up to thousands of kilometres from the area where they are formed.

Atmospheric particles are characterised by various shapes: from the rough-edge shape of a crustal particle (Figure 2a), to the long branched chains of small nanoparticles characterizing Diesel exhausts emission

(Figure 2b), to the flat appearance of a skin fragment (Figure 2c), to the cubic shape of a sodium chloride crystal (Figure 2d).

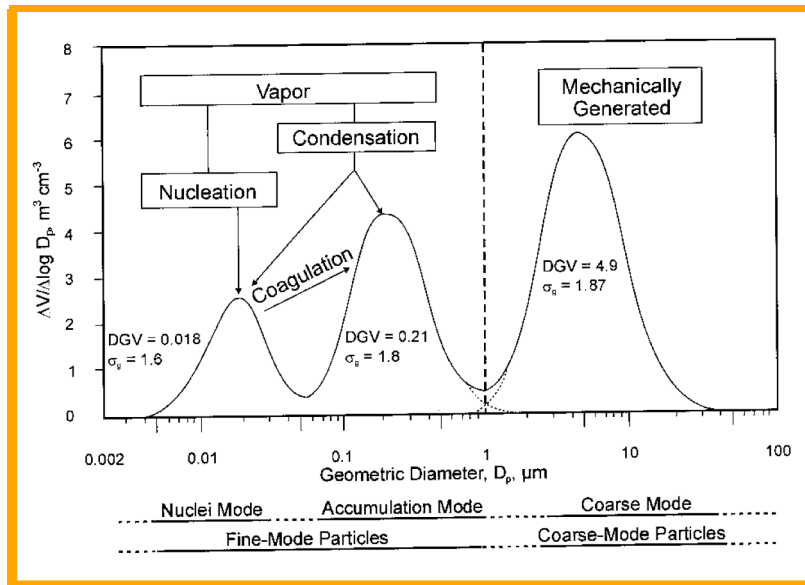


Figure 1: Typical size distribution of atmospheric particles.

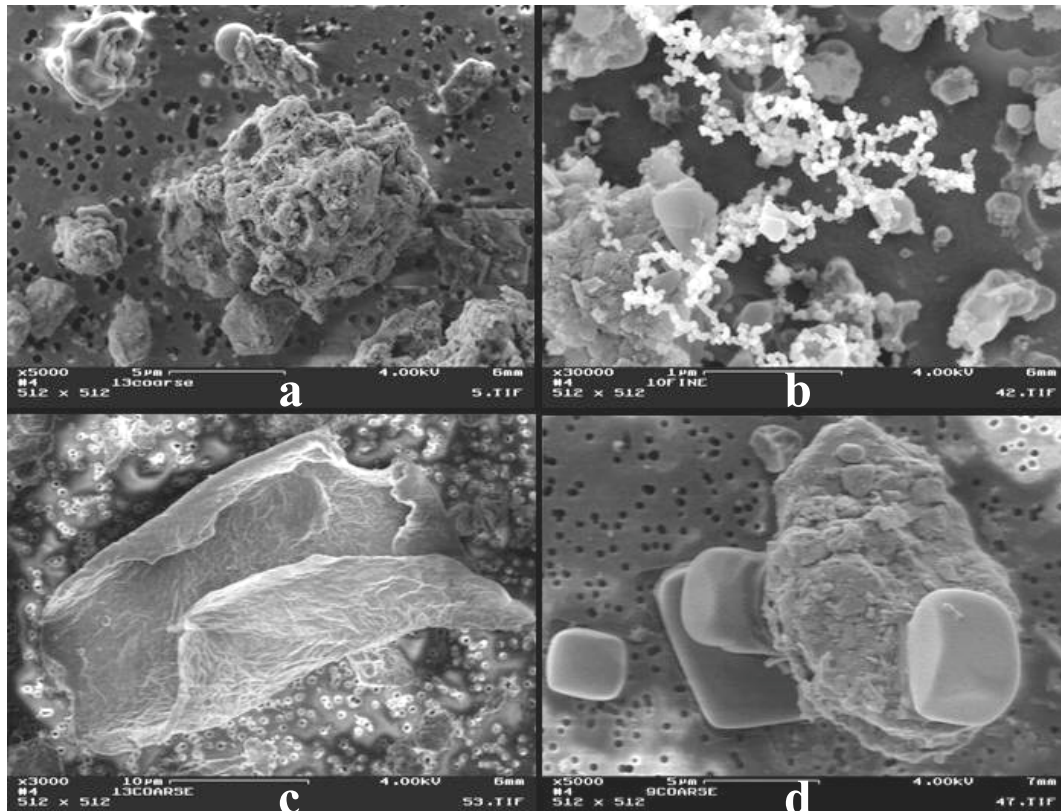


Figure 2: Shapes of atmospheric particles. Photos by courtesy of Prof. Y. Mamane, Technion, Haifa (Israel).

## 2 SOURCES AND EFFECTS

Sources of particulate matter can be natural or anthropogenic. Naturally occurring particles are produced by volcanoes, sea spray, grassland fires, desert dust and by a variety of biological sources (pollen, bacteria, fungal spores, fragments of vegetable organisms and of animals). Anthropogenic particles derive from human activities, such as the burning of fossil fuels in vehicles, domestic heating, power plants and industrial processes. Averaged over the globe, anthropogenic PM accounts for about 10% of the total aerosol amount. According to its source, PM has a different chemical composition. For example, wind-blown mineral dust tends to be made of mineral oxides and other material blown from the earth's crust, sea spray, considered the second-largest contributor in the global aerosol budget, reflects the composition of sea water and consists mainly of sodium chloride, car exhausts mainly emit elemental carbon. A relevant fraction of atmospheric PM is constituted by secondary inorganic particles, which mostly derive from the oxidation of primary gases such as sulphur and nitrogen oxides, leading, respectively to sulphuric and nitric acid; in the presence of ammonia, these species form ammonium salts (ammonium sulphate and ammonium nitrate). Secondary organic particles, instead, may be formed from the reaction (mainly oxidation) of biogenic emitted species (volatile organic carbon compounds).

It is widely recognised that atmospheric PM influence climate through at least two main pathways: its effect on both the absorption and scattering of solar radiation and its role in cloud formation processes. The interaction of aerosol particles with the solar radiation depends on its chemical composition. For example, elemental carbon is one of the most important aerosol species absorbing solar radiation, while sulphate exhibits the opposite behaviour. The ability of the atmospheric aerosol to influence the way solar radiation is transmitted through the atmosphere has relevant consequences in terms of radiation budget and thus in terms of climate change.

PM deposition exerts a significant influence on aquatic and terrestrial ecosystems. Deposition of acid pollutants such as sulphuric acid contributes to soil acidification with adverse effects on forests and crop cultivation and on the economy. Enhances rates of nitrates deposition, instead, contributes to the eutrophication of aquatic ecosystems, causing a negative impact on the life of aquatic animals.

The effects of PM on human health, widely studied in the last twenty years, include asthma, lung cancer and cardiovascular issues. A sound relationship has been found between current  $PM_{10}$  concentration in ambient air and the number of hospitalizations and deaths due to respiratory and cardiovascular diseases. The threat of atmospheric particles to health depends on their size, shape and, again, chemical composition. The size of a particle determines the portion of the respiratory tract where it will rest when inhaled:  $PM_{10}$  is able to penetrate in the bronchi,  $PM_{2.5}$  in the lung and nanoparticles are able to pass through the lungs and enter the circulatory system (Dockery and Stone, 2007; Perez et al., 2009).

## 3 CHEMICAL COMPOSITION

During recent years, substantial improvements have been carried out in the chemical characterisation and identification of the main atmospheric aerosol components (Viana et al., 2008). All the individual inorganic species typically representing more than 1% of the total PM mass can be easily determined and their main sources identified: crustal elements (silicon, aluminium, iron, calcium, carbonate), sea-salt aerosol (sodium chloride), inorganic secondary species (nitrate, sulphate ammonium), primary anthropogenic species (elemental carbon).

Much more complex is the situation for organic compounds, as this class constitutes a relevant fraction of PM mass (20 – 60%) but includes a wide variety of individual species, each one at very low concentration level. Organic matter can be measured as a whole, but only a small part of the species that constitute this group can be determined individually; this is the reason why the monitoring of organic species in PM is generally addressed only to harmful (toxic and carcinogenic) compounds or to specific species that can be considered as tracers of specific PM emission sources.

A reliable sampling procedure for the determination of PM chemical composition involves the simultaneous collection of a specific PM size fraction (e.g.  $PM_{10}$  or  $PM_{2.5}$ ) on one Teflon and one quartz filter membranes. After the sampling, the PM mass concentration is determined on the Teflon filter by the gravimetric procedure or by an equivalent method such as the beta attenuation method. Quartz filters are

analysed for their elemental carbon and organic carbon content (EC/OC) by means of a thermo-optical analyser. Teflon filters are analysed for their metal content (Al, Si, Fe, Na, K, Mg, Ca, S and some microcomponents) by energy-dispersion X-ray fluorescence, a non-destructive technique; then they are extracted and analysed for their anionic ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) and cationic ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$ ) content by ion chromatography. Following this procedure, the main component of the collected particulate material can be identified and quantified and a general picture of the aerosol composition obtained (Perrino et al., 2007, 2009).

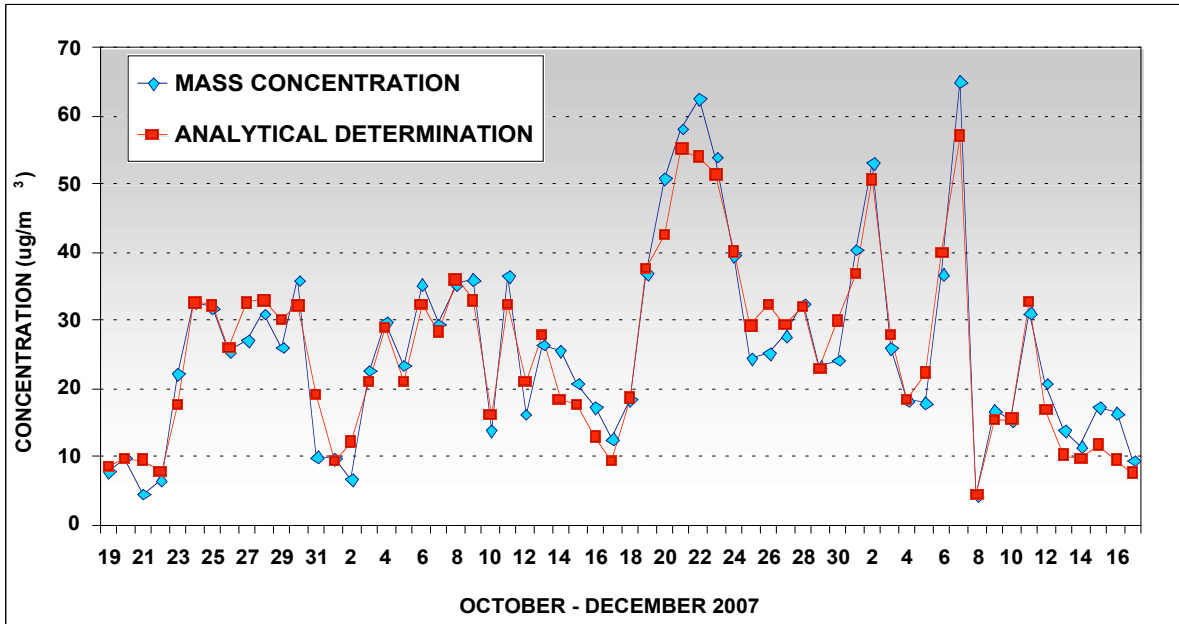


Figure 3: Comparison of daily PM<sub>10</sub> concentration obtained by the gravimetric determination of the collected mass and by the analysis of individual macro-components. Sampling area was a peri-urban site in the vicinity of Rome.

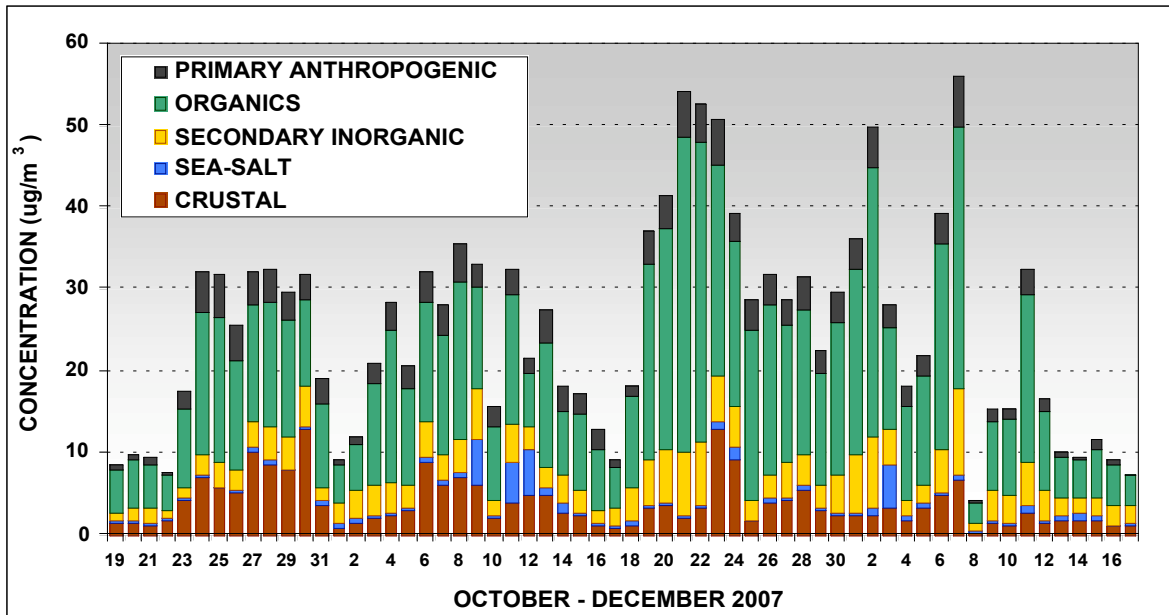


Figure 4: Daily chemical composition of PM<sub>10</sub> at a peri-urban site in the vicinity of Rome.

The comparison between the PM<sub>10</sub> mass and the sum of the individual macro-components is shown in Figure 3 for a series of daily samples collected in a peri-urban area in the vicinity of Rome during the winter of 2007. The chemical analysis of macro-components allowed the reconstruction, on average, of about 98% of the PM mass.

To have a comprehensive view on the main sources of PM, the main chemical components (ions, elements, elemental carbon and organic carbon) can be grouped into five classes, which reflects the five main PM sources: soil (crustal components), sea, combustion (primary anthropogenic compounds), atmosphere (secondary inorganic pollutants) and biosphere (organics). The contribution of soil is calculated by adding the concentration of elements (as metal oxides) generally associated with mineral dust (Al, Si, Fe, K, Ca, Mg and Na oxides); sea-salt is calculated from the concentration of soluble sodium and chloride and of minor sea-water components (sulphate, magnesium, calcium, potassium); the contribution of combustion sources is mainly constituted by elemental carbon; non-sea-salt sulphate, nitrate and ammonium constituted the secondary inorganic fraction; organic matter (organic carbon multiplied by a factor that takes into account the non-carbon content of organic molecules) constitute the contribution of the biosphere (Perrino et al., 2009).

The day-by-day concentration of these five groups of components during the same study shown in Figure 3 is reported in Figure 4. The average composition during the whole year 2007 is shown in Figure 5.

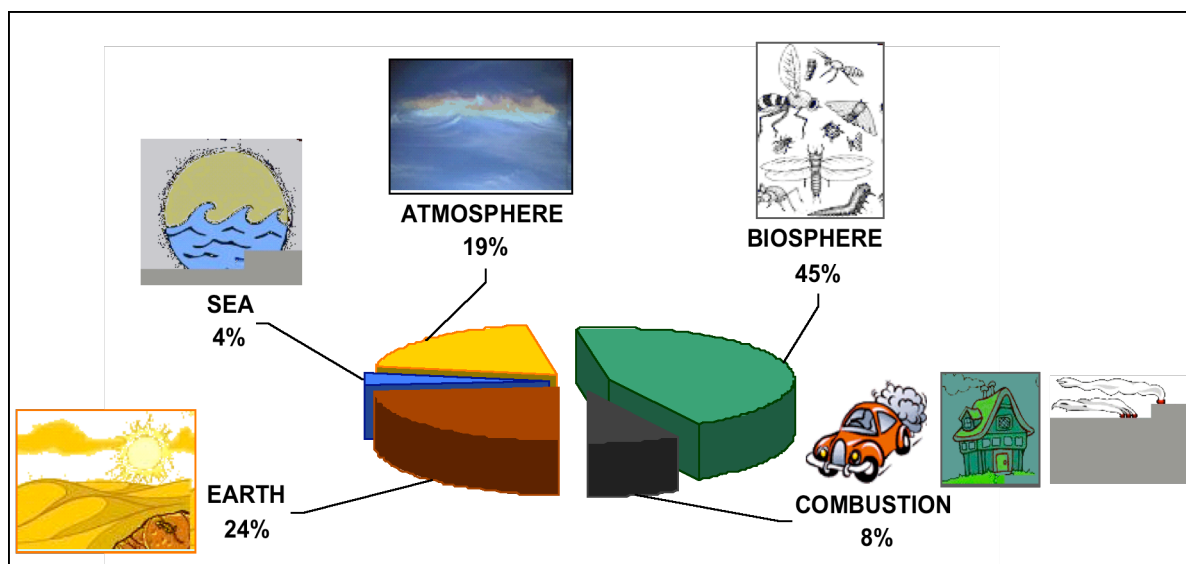


Figure 5: Average chemical composition of PM<sub>10</sub> during 2007 in a peri-urban site in the vicinity of Rome.

PM composition shows a wide variability in space and time. In North-African arid regions, for example, the contribution of soil may exceed half of the total PM<sub>10</sub> mass even on a monthly basis, while Italian coastal regions may experience daily sea-spray contributions up to 30 – 40%; the concentration of primary anthropogenic components steadily decreases when moving from traffic sites or industrial areas towards urban background, semi-rural and regional background location, while the distribution of secondary compounds, due to their peculiar formation mechanism, is almost homogeneous over a regional scale. In Italy, the contribution of crustal matter increase during the spring and the summer, due to more frequent Saharan dust intrusions and to the higher dryness of the soil that enhance particle re-suspension, while the contribution of organics increase during the warm period.

The relevance of one of the main sources of organic particles can be estimated by determining levoglucosan, a sound and specific tracer of the emission from domestic wood burning. Levoglucosan is a monosaccharide derivatives produced by the thermal degradation product of cellulose. The molecule is stable and emitted at such high concentrations (11-17% of the total emitted organic carbon) that it can be detected at considerable distances from the original combustion source; moreover, it is produced by the combustion of hard wood and not of leaves. For all these reasons, levoglucosan can be considered a reliable tracer of residential wood burning (Simoneit et al., 1999).

Atmospheric pollution studies have shown that levoglucosan represents a remarkable fraction of organic matter (up to 10%) and that the emission from residential wood burning may constitute up to more than 80% of the total organic carbon in atmospheric particulate matter. The highest concentrations of this species are recorded during the winter period: in particular, at sites when domestic biomass burning is supposed to be relevant, the winter-to-summer ratio is very high (30-40) while it is about one order of magnitude lower at sites assumed not to be directly influenced by domestic biomass burning. Also, it has been highlighted that the difference between the winter and summer average concentration of organic carbon is very close to the difference between winter and summer estimation of domestic biomass burning contribution. In other words, the emission from fireplace combustion seems to be, by far, the main responsible for the increase of organic carbon atmospheric concentration during the winter. For example, the data reported in Figure 6, which refer to a one-month study carried out in a location sited inside an Alpine valley, show that biomass burning was the most important source of both PM<sub>10</sub> and PM<sub>2.5</sub> during the winter period, and that most of the seasonal difference in PM mass concentration (about 25 µg/m<sup>3</sup>) was due to this domestic combustion process.

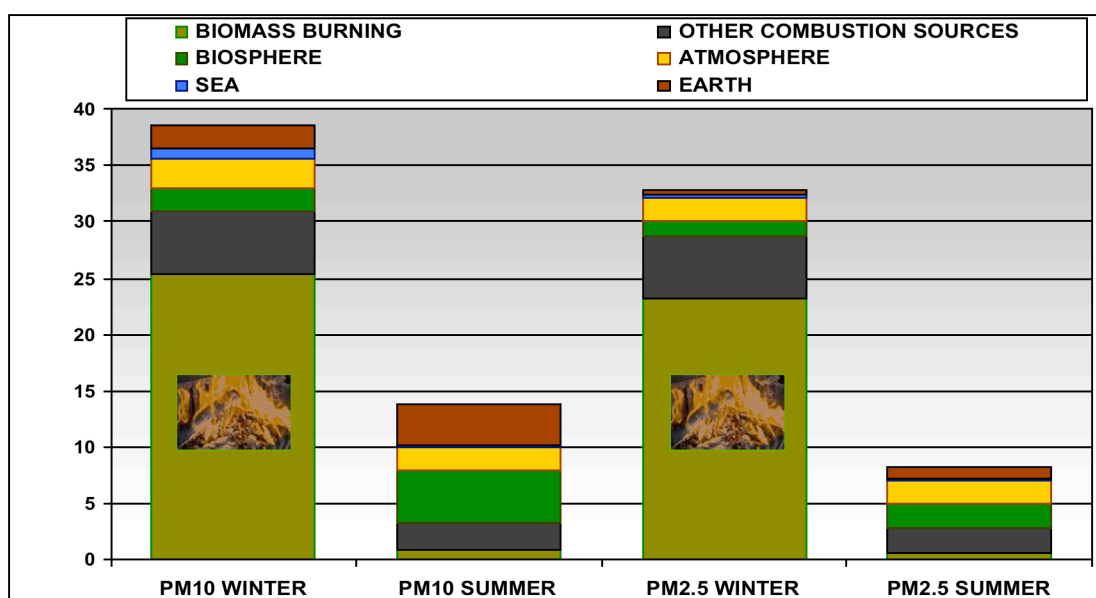


Figure 6: Average chemical composition of PM<sub>10</sub> and PM<sub>2.5</sub> in an alpine valley.

#### 4 DILUTION PROPERTIES OF THE ATMOSPHERE

The knowledge of the dilution properties of the lower air layers is an essential tool for understanding the accumulation of particulate matter and, in general, the time evolution of pollution processes. The atmospheric concentration of any pollutant, in fact, depends not only on its emission, transformation and deposition rate but also on its dilution in the planetary boundary layer. In short, any atmospheric pollution event is the result of a complex interaction between chemistry and meteorology, that is, between the intensity of pollutants production and the capacity of the atmosphere to dilute them (Han et al., 2009; Perrino et al., 2008; Vecchi et al., 2007; Zhang et al., 2009).

We can obtain useful information about the dilution potential of the atmosphere, which is not directly measured by any standard meteorological procedure, by monitoring the natural radioactivity due to Radon short-lived decay products. The emission flow of Radon from the ground, in fact, can be considered as constant in the time and space scale of our observations and Radon air concentration at a given location only depends on the dilution factor. By determining the natural radioactivity due to the Radon progeny we can obtain a reliable picture of the dilution properties of the lower atmosphere.

The study of natural radioactivity 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 the air quality improves. Natural pollution events (desert dust, sea-spray), however, are generally recorded during advection periods.

The example reported in Figure 7 shows how the periods characterised by atmospheric stability (high night-time maxima and high daytime minima of natural radioactivity, e.g.: November 5-7 and 22-25) lead to an increase of PM concentration, while during advection periods (constantly low natural radioactivity values, e.g.: November 7 and 14-16) PM concentration quickly decreases. In general, the shape of the time variations of PM concentration follows the shape of natural radioactivity pattern.

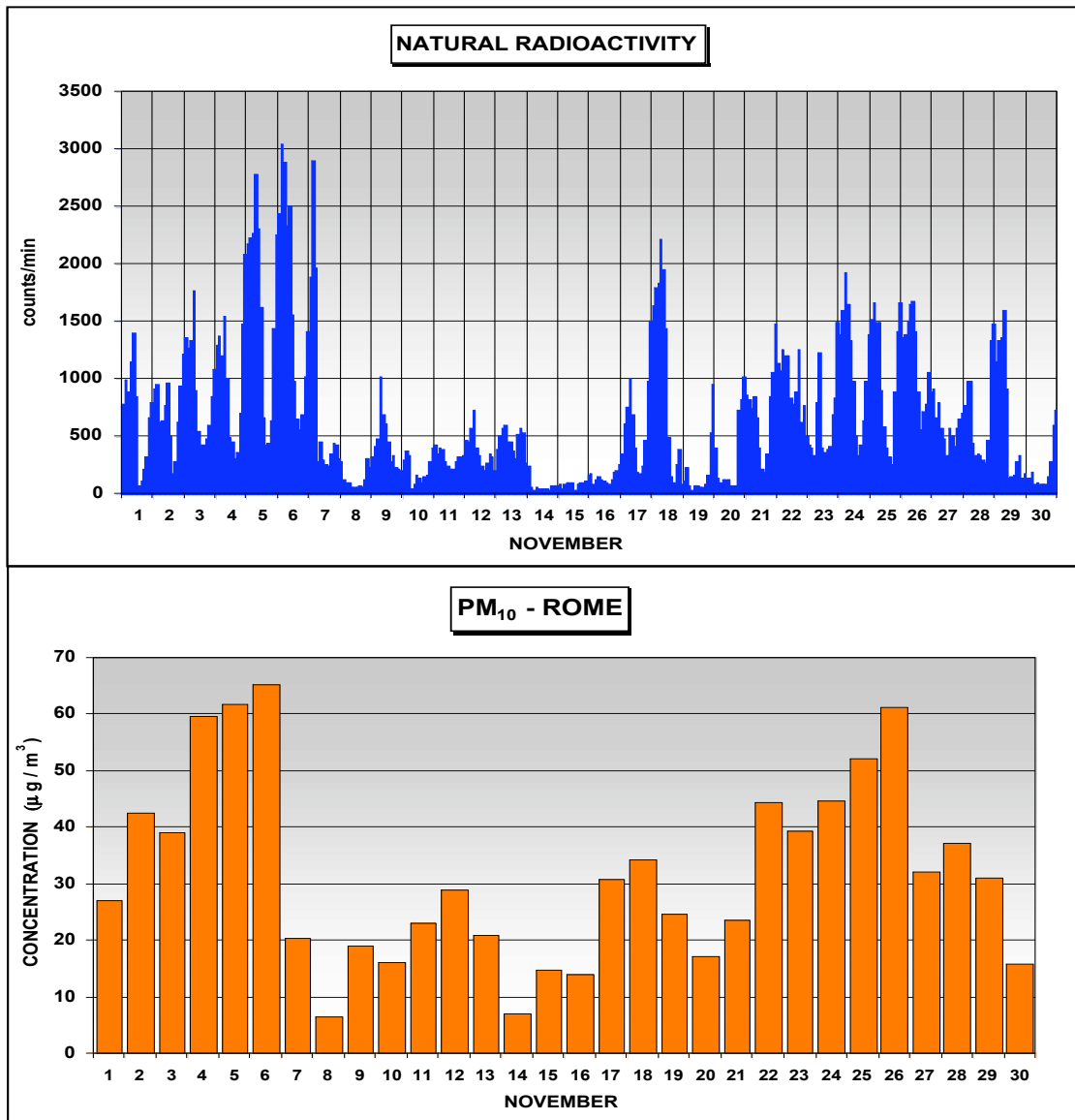


Figure 7: Time pattern of natural radioactivity and PM<sub>10</sub> concentration in Rome.

In order to make the information contained in the pattern of natural radioactivity more easily perceived and interpreted, a Daily Dilution Index, able to characterise each day in terms of meteorological predisposition to the occurrence of a pollution event, has been developed. The Index is a proper combination of natural radioactivity values and of their time derivatives during the times of the day that favour the occurrence of PM



pollution (early morning and evening). The data in Figure 8 show that the Index is very efficient in tracing  $PM_{10}$  concentration variations, demonstrating that the dilution properties of the atmosphere is a driving factor in determining pollution events (Perrino et al., 2009).

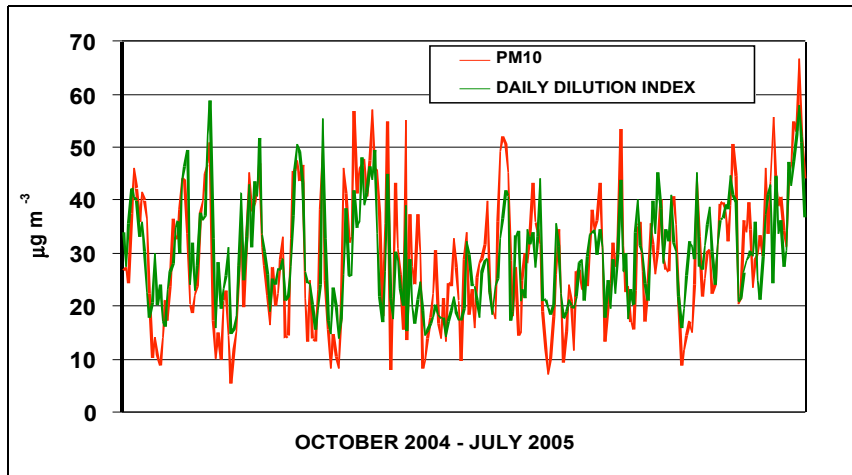


Figure 8: Comparison between Daily Dilution Index (based on natural radioactivity data) and  $PM_{10}$  concentration.

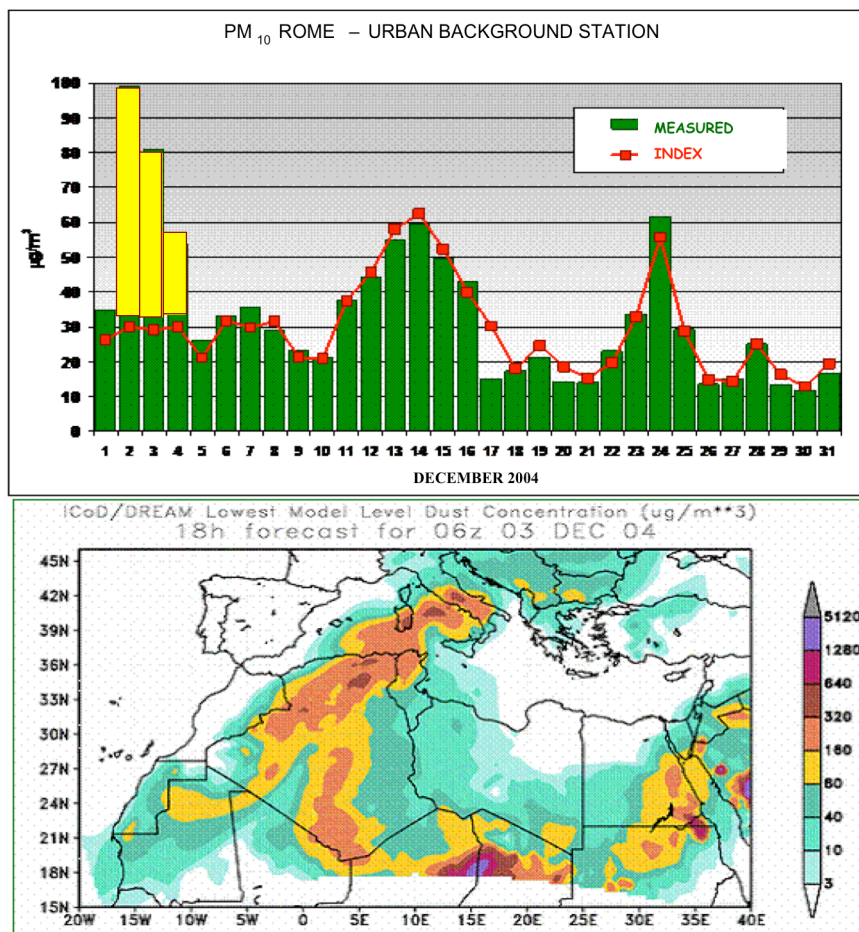


Figure 9: Daily Dilution Index and  $PM_{10}$  concentration in Rome (upper panel) during a desert dust episode, shown by the results of the DREAM model simulations (lower panel).



The monitoring of natural radioactivity can be used also to evaluate the contribution of natural events to PM concentration. The identification of natural events is of particular importance, as the European Directives addressing the limit values for particulate matter provides that days when PM<sub>10</sub> and PM<sub>2.5</sub> limits are exceeded because of natural events should not be considered in the computation of both the annual concentration value and the exceedances of the daily concentration value.

Taking the case of Central Italy, one can observe that sea-spray aerosol is generally a minor constituent of PM<sub>10</sub> (1-3%) and even during the transport of air masses from the sea the increase in PM<sub>10</sub> mass concentration due to these compounds does not generally exceed 10 ug/m<sup>3</sup>. Crustal components, instead, generally constitute 10-20% of the PM<sub>10</sub> concentration, and during desert dust events the contribution of these species to PM<sub>10</sub> may even exceed 100 ug/m<sup>3</sup>. As a consequence, episodes of dust transport from the African desert, although not frequent, may easily cause exceedances of the limit values.

During the desert dust intrusion of 2-4 December 2004, shown in Figure 9, PM<sub>10</sub> concentration at the urban background station in Rome reached values close to 100 ug/m<sup>3</sup> (upper panel). The lower panel of Figure 9 reports the results of the simulations run by the DREAM model for December 3<sup>rd</sup>. The model, developed by the Euro-Mediterranean Centre on Insular Dynamics (<http://www.bsc.es/projects/earthscience/DREAM/>), simulates the atmospheric circulation of desert dust. The calculation of the Daily Dilution Index, reported in the same graph, was in very good agreement with PM<sub>10</sub> values during the whole month, except, as expected, during the three days of the episode. The values of the Index calculated for these three days are a sound estimate of the PM<sub>10</sub> values that would have been recorded in the absence of the event. The chemical analysis of PM confirmed that the difference between PM<sub>10</sub> concentration and the value of the Index (yellow bars in figure 9) was due to crustal matter, which during this period constituted more than 50% of PM<sub>10</sub> concentration.

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