PM2.5 Size Distribution and Characterization by Carbon Isotope in Tuscany (Italy)

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This study is focused on the numerical distribution and isotopic description of PM2.5 developed within the PATOS II (Particolato Atmosferico TOScana) regional project about the characterization and source apportionment of atmospheric aerosol (PM2.5) in Tuscany.

PM isotopic analysis can play an important role in the individuation of primary and secondary sources and also in the determination of the natural/biogenic or anthropogenic/combustion contribution to the measured concentration. In addition, the PM2.5 particle number concentrations and the relative contribution of ultrafine particles are interpreted to identify the emission sources, the main atmospheric processes and the factors related with the dispersion of atmospheric pollutants.

The analytical results in term of $\delta^{13}C$ parameter show a greater variability in the urban and suburban background sites than in the urban traffic site, where the $\delta^{13}C$ parameter does not vary significantly: this could be strictly correlated with traffic emissions and independently from the total particles number. On the contrary, urban and suburban background sites are affected by the meteorology and atmospheric processes. For this reason we can observe a wider variability in the $\delta^{13}C$ values due to the contribution of different emissions sources. Despite all, in urban background we can observe lower $\delta^{13}C$ values related with high number of total particles; this effect could be related with a traffic emission transport, because the $\delta^{13}C$ parameter is similar to the $\delta^{13}C$ value of urban traffic sites.

1. Introduction

Particulate Matter (PM) is one the most important pollutant monitored for the air quality assessment and in particular PM2.5 have direct effects on human health. European Directive 2008/50/CE describes new guidelines about air quality and PM2.5 reduction policy. Despite all many national and regional governments have not reciped the normative in the internal environment laws and PM2.5 problems remain. The problems are focused on urban areas where there are many pollution sources (transports and industrial activities) and particular climatic and geographic conditions.

In fact PM2.5 pollutant deals with a wide range of sources either anthropogenic, natural or "secondary", as well as with climate and meteorological phenomena. The complex mixture of inorganic and organic compounds, both present in the particulate matter composition, is one of the main aspects to be taken into consideration for both their characterisation and the sources emissions apportionment. Other important parameters to be taken into account are the morphology and dimensions of the particles. The shape and the dimension of the particles have a direct interaction with their nature and the risk assessment on human health. Due to the different possible formation pathways (chemical reaction in atmosphere, nucleation, condensation, coagulation and cloud processes) of the secondary PM, it shows different shapes and a wide range of dimensional distribution. It is known (Raes, 2000) how the microphysics processes of particles formation and evolution could generate particles from 10 nm to 10 μm with very different chemical composition.

Stable carbon isotopes are a strong instrument for tracing PM source emissions and process in areosol and atmospheric particles generation. Through stable carbon isotope analisys it is possible to differentiate anthropogenic and natural particulate carbon emission and discriminate road traffic from industrial sources.

This study is carried out within the PATOS II (Particolato Atmosferico TOScana) regional project about the characterization of atmospheric aerosol (PM2.5) in Tuscany and it is focused on the size distributions and PM 2.5 carbon isotopic analysis of samples collected in three different sites.

2. Materials and Methods

2.1 Monitoring Sites

Monitoring campaigns have been performed at three sites in the Tuscany Region characterised by different source exposure. A short description of each site and of its exposure to the emissions is reported in Table 1. Two of the selected monitoring sites were located in Firenze, FI-Gramsci Urban/Traffic (FI-UT) and FI-Bassi Urban/Background (FI-UB); the third site was located in Livorno, LI-Maurogordato Suburban/Background (LI-SB).

Table 1 Monitoring sites description

Site	Site description	Site exposure
FI-Bassi	Urban Background	Not directly expose to traffic
FI-Gramsci	Urban Traffic	Directly exposed to traffic emissions of a two-way, double carriageway street
LI-Maurogordato	Suburban Background	Not exposed to traffic, but near to an industrial area

The sampling campains cover the period spring 2009 - spring 2010. The results discussed below refer to summer and autumn 2009 period; the final analyses (including winter 2009 and spring 2010) are in progress.

The Grimm monitoring has been performed to three weeks in all monitoring sites for each season. Isotopic analyses have been carried out at the same time of Grimm data analyses, but limited at one week for each three weeks sampling period.

2.2 Instruments

A Low Volume Sampler (LVS), Tecora TCR, with sampling head USEPA-cfr part.50 for PM2.5 with operating flow rate of 16.7 liter/min was used for collecting every two days (48hr) aerosols samples on quartz fiber filters Ø47 mm of Ø 0.4 μm equivalent porosity. For the isotopes determination the PM2.5 filters were divided into small pieces (> 3) to have different replicates of the same sample. The PM2.5 filter pieces were weighted into a balance, Sartorius CP225D-OCE (10μg weight resolution), and prepared for the analysis by inserting each of them into a tin capsule (average weights 25-35mg). Samples were flash-combusted with a Carlo Erba Elemental Analyzer (Thermo-Finnigan EA-1108); organic matter was converted to CO_2 in a quartz column with a specific oxidizing catalyzer (Ag/Co oxide, Cr oxide) at 1020°C, and then passed over a reducing column (Cu oxide and Cu) at 650°C in a helium stream. The produced CO_2 was introduced into the mass spectrometer (Thermo Finnigan-Delta Plus XP) for the determination of the isotopic abundance by continuous flow using the CONFLO III. A series of reference standard (graphite and sucrose) was analyzed to monitor data reproducibility.

Simultaneous monitoring of fine particles' presence (from 300nm up to 20 μm of diameter) has been performed by a Grimm model 1108 particle size analyser. This optical analyser uses light-scattering technology for single-particle counts, whereby a semiconductor laser serves as the light source. The scattered signal from the particle passing through the laser beam is collected at approximately 90° by a mirror and transferred to a recipient photo diode. After reinforcement, the signal passes a 15-channel signal analyser and is finally classified in the corresponding size range bin, where the incoming signal is counted. The ambient air to be analysed is drawn into the measurement cell by means of an inhalable sampling head at a flow rate of 1.2 l min^{-1}. During the monitoring campaigns, 1-min averaged number concentration data have been recorded on a data storage card: 24-h averaged size distributions have been subsequently calculated based on the resulting data.

3. Results and Discussion

The investigated size Grimm range for particles' number concentration is within the interval 0.3–20 μm, even though the main focus of the work is on the submicron size range, where almost 99% of the particles falls.

Particle size distributions, averaged number concentration in summer and autumn are plotted in Fig. 1 for the three sites considered. All the distribution functions show a similar pattern: in the log-log scale plot, the concentrations of particles are caracterized by two parts almost linearly decreasing for increasing diameters, connected with an about constant segment. As already reported for the typical size distributions in the urban environment (Seinfeld and Pandis, 1998), this corresponds to a bimodal distribution for both seasons.
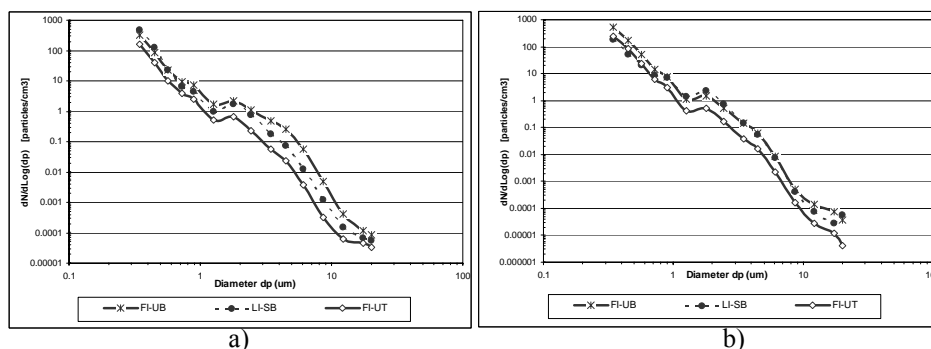
Fig. 1- Observed size distribution for number concentration in a)summer, b) autumn

The distributions appear to be quite similar for the three sites monitored. The bimodal distribution shows a first peak at 0.35 μm and another around 2μm. In summer the three stations show a larger number of particles in classes with diameters larger than 2.5 μm, while in autumn the difference is visible between suburban and traffic stations.

Relating size distribution to the carbon isotope results no correlation has been found; this could be due to the fact that the size distribution don't shows substantial differences among the three sampling sites and seasonal period too. For this reason carbon isotope results have been plotted versus total PM2.5 particles number measured by Grimm. In this respect Fig. 2 (δ^{13}C value vs. PM2.5 particles number) shows that the δ^{13}C value is not related with the particles number. However, we can observe in particular that the δ^{13}C value of FI-UT samples is comprised between -25.5 and -26.1; it is typical of traffic sources and the lower standard deviation could confirm that the contribution of traffic sources is concentrated in the fine fraction of particulate matter.
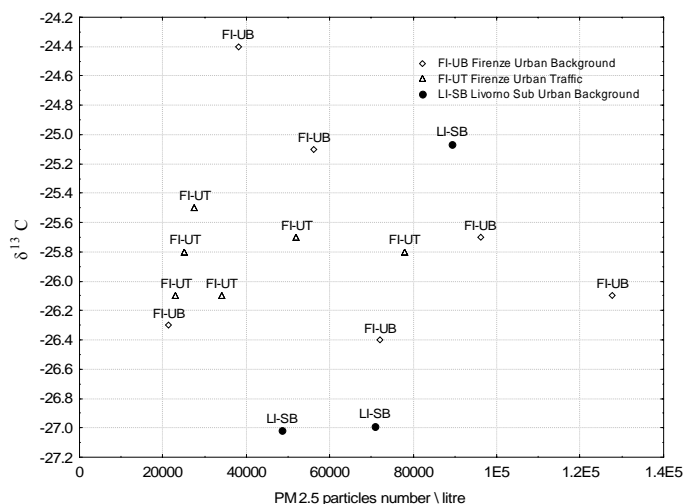

Figure 2- δ^{13}C value versus total PM2.5 particles number

In general, background and suburban sites depend on the meteorology and atmospheric processes; for this reason we can observe a wider variability in the δ^{13}C values relating to the changing in the contribution of different source emissions. Actually, a slight correlation is obtained in Firenze Urban Background where the δ^{13}C value is more

negative with the increase of particles number. In this case, a major particles number could be attributed to traffic dust transport from the centre to the border zone of the city, where the background station is located.

In order to recognise the contribution of different sources the PM2.5 PaTOS isotopic analysis have been related to the results of a study on PM carbon isotope characterization in Paris.

Fig.3, δ^{13}C vs. carbon concentration plot, discriminates between several carbon sources (Widory et al., 2004) and shows large fluctuations of carbon content among which several trends appear. The FI-UT δ^{13}C values are comprised between unleaded and diesel values, regardless of carbon concentration and seasonal variation, putting in evidence that the main origin of particulate is traffic source. On the contrary, the urban background site (FI-UB) registered highest values of δ^{13}C with low carbon content. This aerosol behaviour is due to the contribution of different sources. In urban and suburban background sites it is possible to observe that the carbon concentration is higher in autumn and decreases during the summer. Especially during the summer we can recognise a -24.5‰ δ^{13}C value which may be ascribed to emissions from geological sources (Lopez-Veneroni, 2009), and -25.0‰ δ^{13}C values and low carbon concentration which could be associated with either a crustal or biogenic sources.
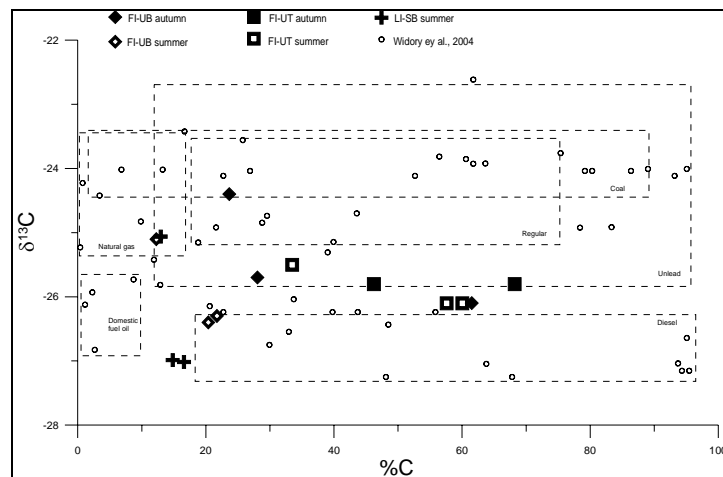

Figure 3-Carbon-isotope characterization of different type of source and sites monitoring.

The lowest δ^{13}C values (-27.0‰) have been detected in Livorno Suburban Background Maurogordato. These results could be related with the nearness of the Agip Oil Refinery and attributed to industrial combustion processes of aromatic compounds.

4. Conclusions

The first values of carbon isotopic analyses relating to dimensional particles measurements in three sites located in Firenze and Livorno, respectively urban traffic

station and urban background in Florence, and suburban background in Livorno, leads to the following results:

- the particles size distribution is a *bimodal distribution* regardless of the location of sampling site and the sampling period;
- in urban traffic site the $\delta^{13}C$ value is not correlated with size distribution and PM 2.5 particles number and the $\delta^{13}C$ value is typical of traffic source despite all seasonal variation too. This could confirm that the contribution of traffic sources is concentrated in the fine fraction of particulate matter;
- slightly correlation among particles number and $\delta^{13}C$ value has been observed in urban background site. Infact the $\delta^{13}C$ value becomes more negative while particles number increases, a transport of traffic dust from the centre of the city to the background site could be justify these $\delta^{13}C$ values.

In conclusion the use of isotopes for understanding airborne pollution and dimension numerical distribution analysis of PM2.5 could provide more information about source apportionment and sites particulate characterization.

References

Lopez-Veneroni D., 2009, Atmospheric Environment 43, 4491-4502.

Raes F. et al., 2000, Atmospheric Environment 34, 4215-4240.

Seinfeld J.H., Pandis S.N.,1998, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. Wiley, NY, USA, pp. 408–442.

Widory D., Roy S., Le Moullec Y., Goupil G., Cocherie A., Guerrot C., 2004, Atmospheric Environment, 38, 935-961.