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PM Characterization by Carbon Isotope

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Isotopic characterization of PM 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. As the matter of fact, a methodology to analyze the stable isotope of the carbonaceous fraction of PM10 has been developed.

The PM10 samples were collected during the PaTOS monitoring campaign Autumn 2005 – Spring 2006 in six sites located on the regional Tuscany territory: Arezzo Urban/Traffic (AR-UT), Lucca Urban/Background (LU-UB), Livorno Suburban /Background (LI-SB), Prato Urban/Traffic (PO-UT), Firenze Urban/Background (FI-UB) and Grosseto Urban/ Background (GR-UB). A Low Volume Sampler (LVS), Tecora TCR, was used with sampling head USEPA-cfr part.50 to collect 24 hr daily aerosols samples on QUARTZ fibre filters.

The PM organic matter on the quartz fibre filters is converted into a combustion apparatus, Thermo Finnigan, Elemental Analyser-EA1108 , into CO_2. A mixed flow rate of helium and oxygen was used as carrier gas in the apparatus to send the CO_2 trough the spectrometer, Thermo Finnigan-Delta Plus XP, for the determination of the isotope abundance. The hardware and software connected to the spectrometer allow to determine δ13C(‰) in relation to the PDB reference standard ("Pee Dee Belemite" CaCO3), applying the $\delta^{13}C/\delta^{12}C$ ratio equation.

The PM10 concentrations, calculated as daily averaged values, show a significant variability from the urban to suburban sites varying from 50 μg/m^3 (AR-UT) to 20 μg/m^3 (LI-SB) as averaged concentration on the sampling period and from autumn 60 μg/m^3 (LU-UB) and spring 25 μg/m^3 (LU-UB) periods. Also the PM carbon content, on period average values, shows very different results from site to sites with a minimum in GR-UB of 20% up to the 60% of LU-UB.

In figure 1 the average values of the carbon content, expressed as weight percentage of the PM, versus the $\delta^{13}C$ parameter were shown for each monitoring sites together with the two parameters variability. The analytical results in terms of $\delta^{13}C$'s values are comprised from – 28 and -23 and show significant variation from the traffic and background sites; in fact, in the background and suburban sites (LI-SB, FI-UB and GR-UB) the $\delta^{13}C$'s show a bigger variability than in the urban sites AR-UT, PO-UT, LU-UB, LI-UB were the results don't vary significantly, and this could be well correlated with the constant emissions from traffic. On the contrary the background sites both urban or rural, depending on the meteorology and atmospheric processes, show a wider variability in the $\delta^{13}C$ values relating to the changing in the contribution from the natural, secondary and anthropogenic source emissions.

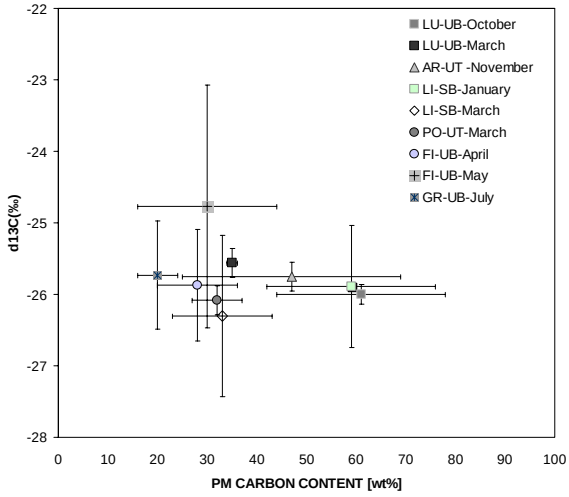

Figure 1. $\delta^{13}C$ [$^o/_{oo}$] versus PM carbon content [wt%] for the monitoring sites, Tuscany.

The lower negativities of the $\delta^{13}C$ values of the PO-UT compared to the AR-UT could be explained by the presence of industrial source that are negligible in the AR-UT and that concurred as lower negative $\delta^{13}C$ values [Widory et al., 2004]. The $\delta^{13}C$ values confirm the indication determined for the identification of the emissions from non stationary combustion sources as traffic vehicles and the differences shown between urban and rural sites [Haung et al., 2006].

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