MAGNETIC ANALYSIS OF ULTRAFINE PARTICLES: APPLICATIONS TO AIR POLLUTION

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The PM_{10} particulate in the city of Torino (Italy) has been investigated by means of a variety of magnetic measurements on the filters collected daily, over a period of six months, at four air-quality monitoring stations run by ARPA-Piemonte and located in different environments (Fig. 1).

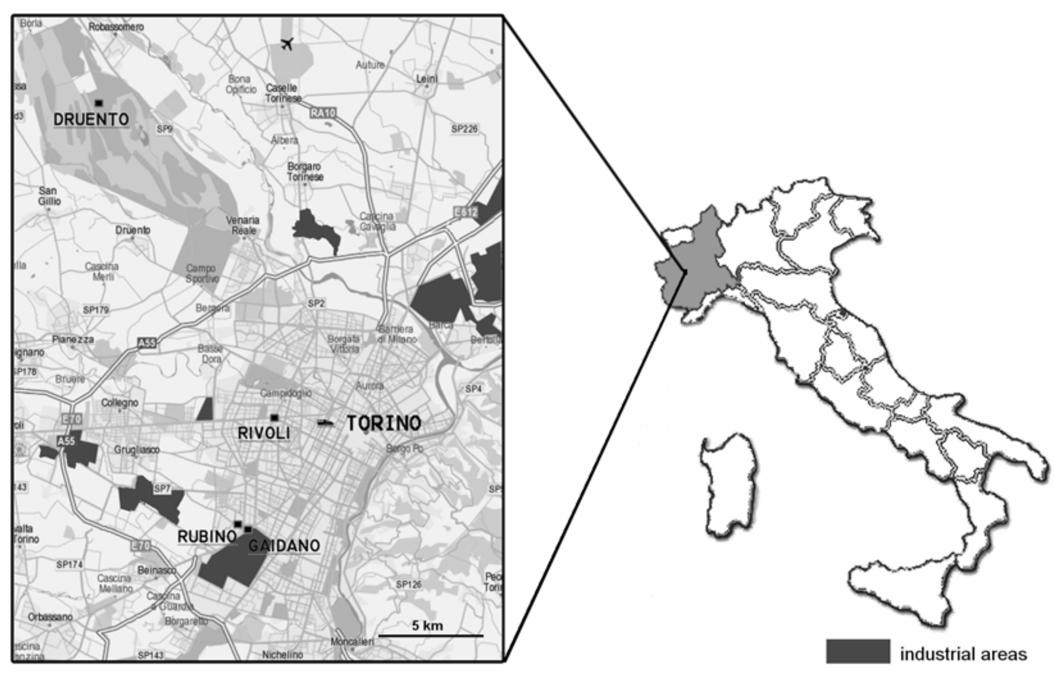

Fig. 1 - Map showing the location of the stations for the air-quality monitoring.

Moreover, Transmission Electron Microscopy and Energy-Dispersive X-ray (TEM/EDX) analyses on samples collected close to two of the four stations supplemented the study.

A standard procedure consisting of Saturation Isothermal Remanent Magnetisation (SIRM) measurements, performed at 77 K and room temperature, was applied to all samples; these analyses were mainly intended to estimate the concentration of different grain-size particles and were focussed on the nanometric fraction. Additional measurements at different temperatures (hysteresis cycles, susceptibility as a function of frequency, IRM and ARM acquisitions, etc.) were performed on selected samples in order to better characterize the magnetic components.

The results show that the PM10 magnetic fraction mainly consists of a low-coercivity, magnetite-like phase and a minor phase with higher coercivity, which probably results from the surface oxidation of the smallest magnetite grains (*e.g.* Fig. 2). The amount of the magnetic fraction is related to the degree of anthropogenic pollution and it is higher in the sites with high vehicle traffic (Table 1). The grains size distribution falls in the single-domain (SD)-superparamagnetic (SP) range and, at each site, it is constant for long

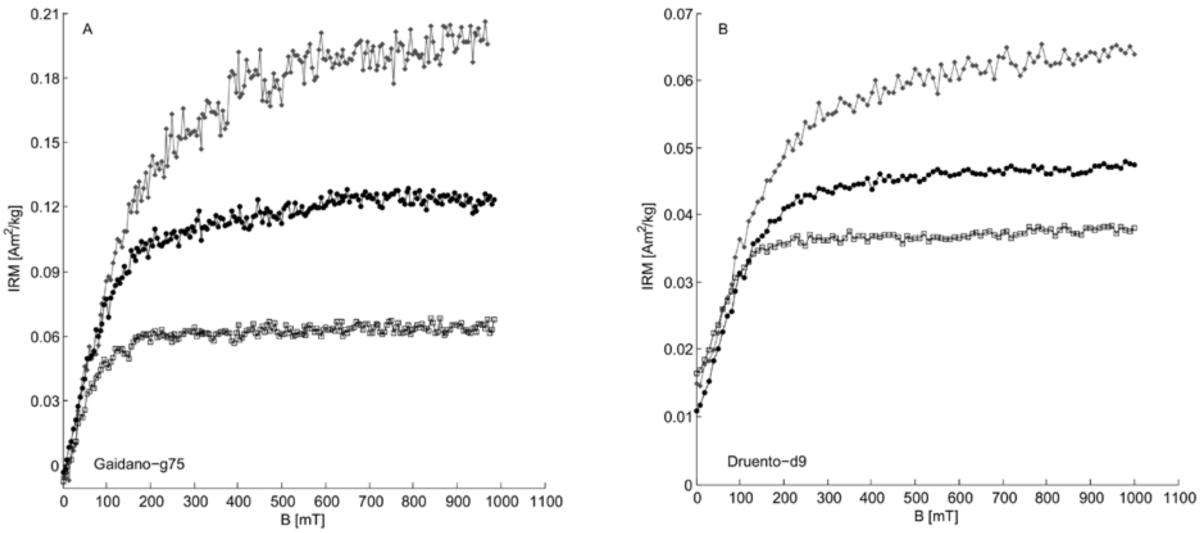

Fig. 2 - IRM acquisition curves at 263 K (square), 77 K (dot) and 15 K (diamond) of samples Gaidano (A) and Druento (B). The 263 K curves show a rapidly saturating magnetization, which points to ferrimagnetic minerals such as magnetite/maghemite; moreover, the broad high-field curvature of the IRM acquisition curves at 15 K, and to a smaller extent of those at 77 K, suggests the presence of a high-coercivity, probably antiferromagnetic phase in addition to the predominant ferrimagnetic mineral. Also the IRM acquired at 15 K is significantly higher than that at 77 K, which is in turn higher than that at 263 K IRM. The large increase of the remnant magnetization measured at low temperatures suggests the presence of a large fraction of ultra-fine SP grains most of which is undetected even at 77 K.

Table 1 - Statistic PM10 concentration and magnetic moment of total magnetic component MTOT of the four stations. PM10, MTOT, are provided as mean, standard deviation, max, min.

Air-Monitoring Station	Type	Number of sample	Sampling period	PM_{10} mean [max-min] (μ/m^3)	M_{TOT} mean [max-min] 10^{-7} Am^2
Durento	suburban park	141	January to June 2007	31 ± 20 [4 - 93]	0.72 ± 0.39 [0.09 - 2.02]
Gaidano	traffic site	136	January to June 2007	52 ± 35 [4 - 133]	3.28 ± 2.37 [0.53 - 10.59]
Rivoli	high-traffic site	177	January to June 2008	53 ± 39 [4 - 179]	4.5 ± 2.73 [1.37 - 15.59]
Rubino	urban park	150	January to June 2008	38 ± 27 [4 - 124]	2.02 ± 1.32 [0.45 - 5.89]

periods of time. The SP particles represent the dominant fraction; they are more abundant in the site with more traffic and decrease moving toward the less polluted sites. At the urban and suburban sites, respectively, about 75% and 60% of the total magnetic signal is carried by SP particles (*e.g.* Fig. 3) with an equivalent spherical diameter less than ≈ 17 nm. The contribution of multi-domain (MD) grains is very small, corresponding to less than 4% of the signal at the urban sites and to about 8-10% at the suburban site.

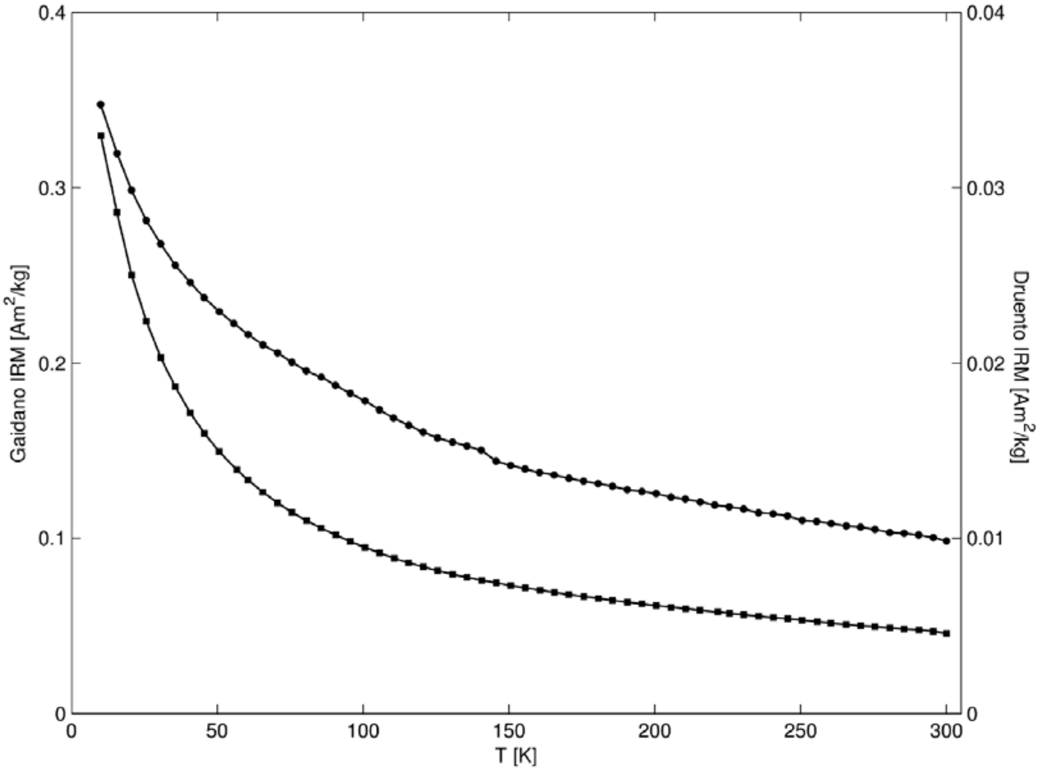

Fig. 3 - IRM *vs*. temperature during thermal demagnetization of the zero field cooling (ZFC) saturation IRM given at 15 K. Samples Gaidano (square) and Druento (dot). The magnetization scale of Druento is expanded by a factor 10 with respect to Gaidano. The general decrease of IRM between 15 K and 300 K confirms the presence of the abundant SP component shown by the IRM acquisition; moreover, the lower slope of the sample Druento, compared to Gaidano, suggests a slightly different grain size distribution of magnetic particles.

Further analyses of morphology, dimensions and chemical composition of the particulate were performed by means of TEM-EDX. TEM observations revealed that most particles were less than 0.5-1 μm in size and EDX analyses show that particles rich in carbon (C-rich) are dominant followed, by S-rich, Si-rich, Fe-rich and Ca-rich particles. Fe-rich particles are mainly composed of small spherical grains (between few nanometer and 60 nm in size) usually arranged in agglomerates (Fig. 4A) and to a lesser extent of larger particles (between 0.1 and 1 μm) with irregular or rounded shape (Fig. 4B). Fe and O are the main constituents of both types of particles; small amount of Mn are always found associated with agglomerate, whereas small amount of Zn and many other element are often found associated with coarse particles.

C-rich and Fe-rich particles of nanometric dimension are more abundant in urban areas and show many similarities. In fact, they have a common source and similar size, they are usually found as aggregates of particles and sometimes they occur together, mixed in the same agglomerate.

Magnetic and TEM/EDX results on mineralogy and size estimation of Fe-rich PM_{10} component are in good agreement and concur to indicate that agglomerates of nanometric Fe-rich particles are the most widespread magnetic pollutant. The joint occurrence of Fe- and C-rich particles points to combustion, and in particular to vehicle traffic, as the main source of PM_{10} ultrafine fraction.

The comparison of the magnetic data with the PM_{10} concentration shows a low correlation between their spatial and temporal distribution (Fig. 5), reasonably due to the small contribution of the magnetic component to the total PM_{10} mass and to the different effects of atmospherical dynamics on their spatial distribution.

On the contrary, a significant correlation occurs between the magnetic signal and several pollutants of

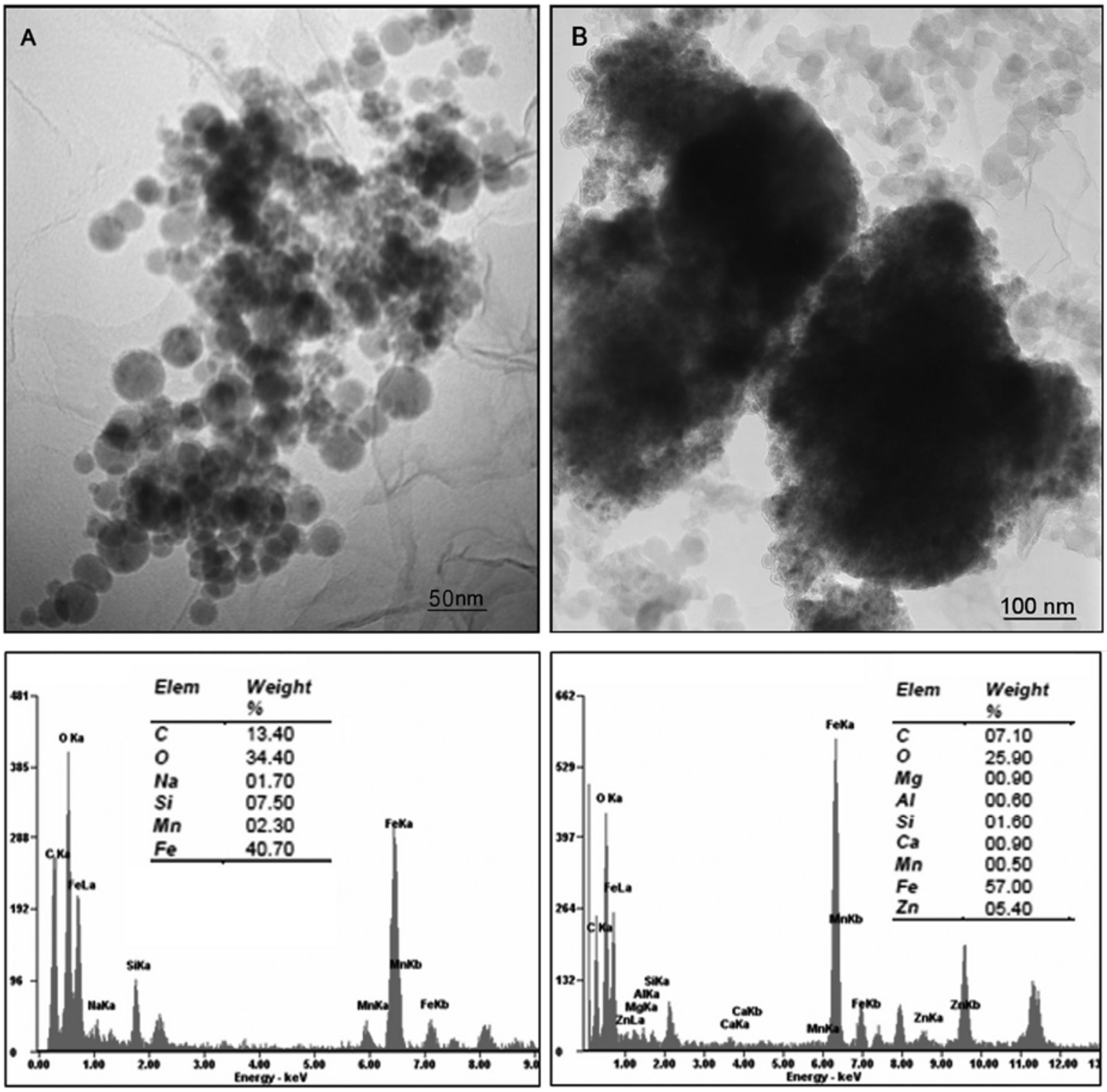

Fig. 4 - TEM images and EDX spectra of typical Fe-rich particles in atmospheric PM_{10} of Turin. (A) Agglomerate of ultrafine particles; (B) individual particles.

anthropogenic origin (PAHs, CO, NO_X, Pb, Cd and Ni; *e.g.* Fig. 5), thus substantiating the anthropogenic nature of the magnetic particles and the hypothesis of a common dominant source, which can be identified in the exhaust emissions of vehicles.

The high correlation between the magnetic component and some common urban air pollutants as well as the occurrence of elements, such as Mn in the Fe agglomerates, highlights the potential use of magnetic measurements to assess the level and distribution of non-magnetic hazardous substances. Moreover, the similarities between the magnetic and the carbonaceous components suggest that magnetic measurements may be a tool to estimate the PM_{10} ultrafine fraction, which mainly consists of C-rich particles.

Our results show that the magnetic technique provides valuable information on local atmospheric pollution, and it can be therefore used as a proxy of the level of anthropogenic pollutants as well as it can significantly contribute to the guidelines of air-quality monitoring.

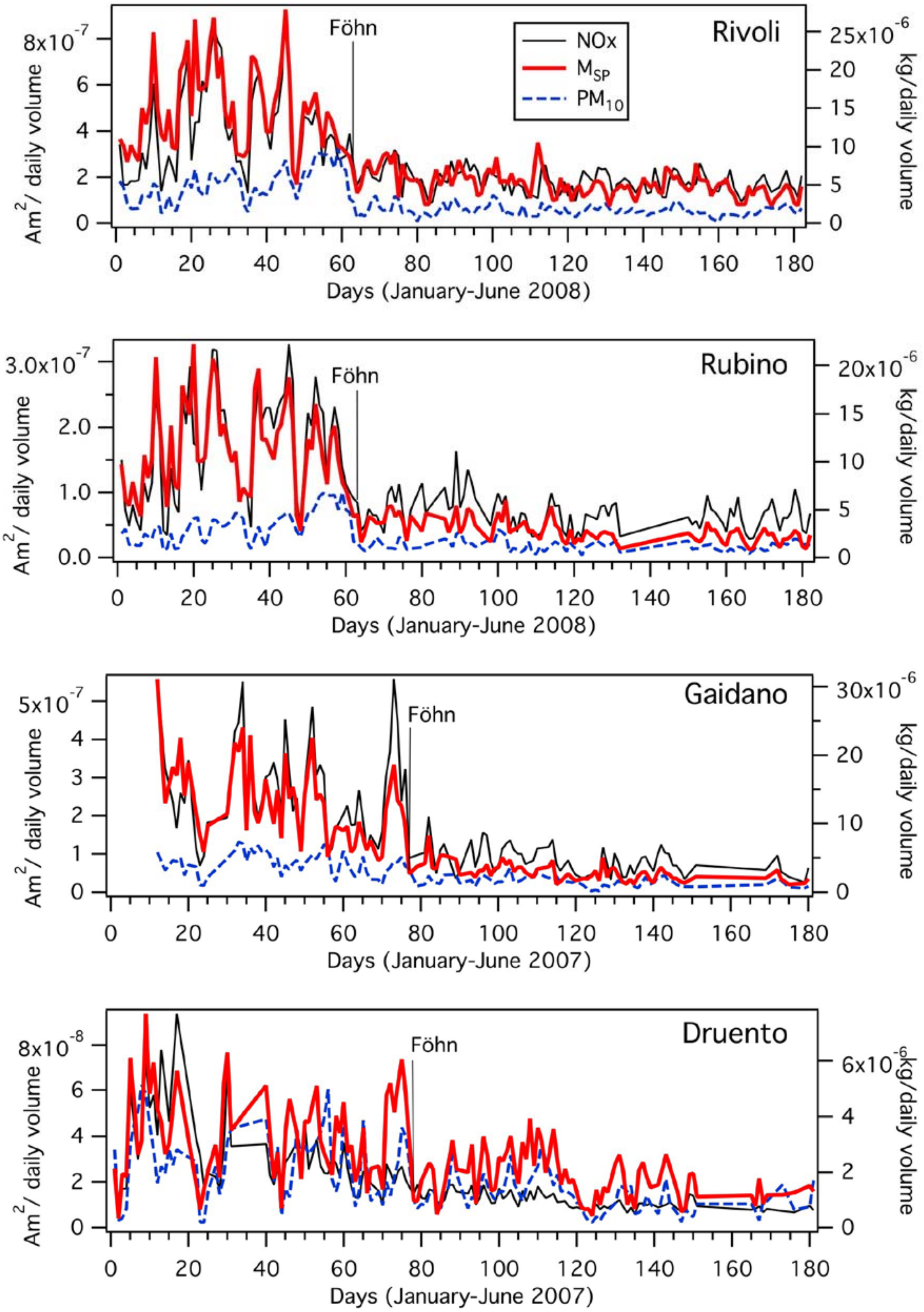

Fig. 5 - Daily variation of NOx and PM_{10} concentrations and magnetic moment of SP component M_{SP}. The curves show a typical situation: the pollutant concentration is higher in the winter season (due to the combination of stagnant atmospheric circulation and increased emissions) and lower in the spring season. The decrease in concentration marked with a thin black line coincides with strong föhn wind on March 19th, 2007 and March 3rd, 2008. NO_x, PM_{10} concentrations are expressed as kg/volume of daily filtered air (55 m^3).