

Chemical characterization of the organic fraction of PM for an urban, rural and remote site in the North of Italy

M. G. Perrone^a, G. Sangiorgi, C. Lo Porto^a, L. Ferrero^a, B. Ferrini^a, Z. Lazzati^a, S. Petraccone^a, B. Darestab^b, G. De Gennaro^b, E. Bolzacchini^a

^a Research Center POLARIS, Department of Environmental Science and Technology, University of Milano Bicocca, Piazza della Scienza 1, 20126, Milan, Italy
^b Department of Chemistry, University of Bari, Italy

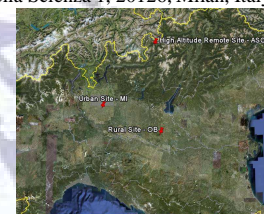
grazia.perrone@uimib.it

SAMPLING SITES AND PM_{2.5} CHEMICAL COMPOSITION

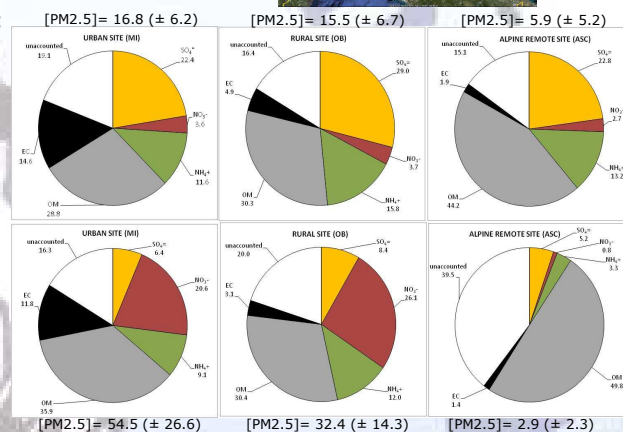
PM_{2.5} was sampled over one year in three sites located in the North of Italy: an urban (Milan-MI; 45°31'19"N, 9°12'46"E), a rural (Oasi Bine-OB; 45°08'40"N, 10°26'08"E) and a high altitude remote site (Alpe San Colombano-ASC, m.2280 a.s.l.; 46°27'18"N 10°18'50"E).

Daily PM_{2.5} samples were collected through a low volume gravimetric sampler (38,33 l/min) for one year, and PM_{2.5} main chemical composition was analysed (Fig.1)

During summer, the high altitude remote site (ASC) is within the boundary layer, and it is influenced by atmospheric transport from the plain. In winter, ASC is above the mixing layer and PM_{2.5} chemical composition is typical of the free troposphere.



SUMMER



WINTER

FIG.1 Mean PM_{2.5} concentrations (± dev.st) and main chemical composition (%).

OM CHEMICAL SPECIATION

Organic matter is an important contribution to total PM_{2.5} mass: 29-36% in the urban and rural site, and up to 44-50% in the high altitude remote site.

OM was chemical speciated for:

- Carboxylic acids: C2-C5 dicarboxylic acids with IC
- n-alkanes: C20-C32 with GC-MS
- Polycyclic aromatic hydrocarbons (PAHs) with GC-MS

		C2-C5 DICARBOXYLIC ACIDS (ng m ⁻³)		PAHs (ng m ⁻³)		C20-C32 N-ALKANES (ng m ⁻³)	
		SUMMER	WINTER	SUMMER	WINTER	SUMMER	WINTER
urban site (MI)		1961.57 (± 166.30)	492.38 (± 52.66)	1.24 (± 0.30)	8.76 (± 0.95)	8.76 (± 0.95)	177.89 (± 55.14)
rural site (OB)		2551.31 (± 124.12)	549.96 (± 245.62)	0.22 (± 0.02)	25.82 (± 4.34)	62.40 (± 13.87)	25.82 (± 4.34)
remote site (ASC)		2532.73 (± 385.22)	478.11 (± 231.92)	0.06 (± 0.04)	7.52 (± 1.39)	7.52 (± 1.39)	0.06 (± 0.04)

TABLE 1 Atmospheric concentrations (ng m⁻³) of trace organic compounds. Mean (± dev.st)

Carboxylic acid concentrations are equally distributed in the North of Italy (MI=OB=ASC) (Tab.1), with higher concentrations in summer than in winter.

PAHs and n-alkanes concentrations are high during winter and they are directly influenced by local anthropic combustion sources with MI > OB > ASC.

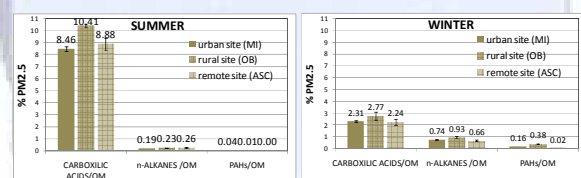


FIG.2 Trace organic compounds as a % of organic matter (OM) in PM_{2.5} samples

CARBOXYLIC ACIDS and SUMMER SECONDARY SOURCE

Carboxylic acids are mainly linked to secondary formation. Oxalic acid (C2: HOOC-COOH) is the most abundant diacid (Tab.2), and C2 concentrations are strictly correlated to longer-chain diacids during summer (R²=0.71-0.93).

		C2 (oxalic acid) ng m ⁻³		C3 (malonic acid) ng m ⁻³		C4 (succinic acid) ng m ⁻³		C5 (glutaric acid) ng m ⁻³	
		SUMMER	WINTER	SUMMER	WINTER	SUMMER	WINTER	SUMMER	WINTER
urban site (MI)		158.7 (± 113.8)	121.8 (± 26.9)	61.3 (± 23.0)	39.5 (± 11.7)	79.9 (± 68.0)	45.6 (± 23.4)	22.3 (± 16.9)	33.1 (± 19.5)
rural site (OB)		137.3 (± 65.3)	88.9 (± 70.1)	47.0 (± 14.0)	32.8 (± 23.0)	45.0 (± 31.0)	18.1 (± 18.6)	12.0 (± 6.7)	18.2 (± 12.2)
remote site (ASC)		292.0 (± 263.3)	107.3 (± 95.2)	201.4 (± 113.1)	117.0 (± 47.3)	97.7 (± 8.5)	72.3 (± 69.6)	36.2 (± 28.1)	9.9 (± 11.5)

TABLE 2 C2-C5 Dicarboxylic concentrations (ng m⁻³). Mean (± dev.st). Percentage of individual diacids to the sum of C2-C5 diacids

Diacid concentrations in summer show a significant dependence to both temperature (exponential function) and ozone (linear function) (Fig.3). The strict temperature dependence of carboxylic acids (dln[]/dT= 0.18 °C⁻¹) would suggest that during summer diacids mainly form from vegetation emissions of OVOCs (Legrand, 2007).

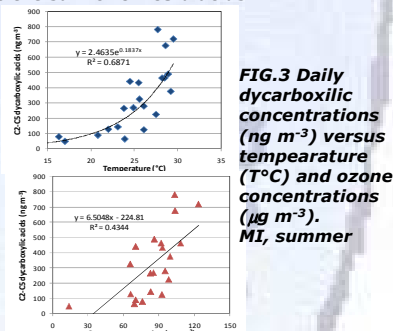


FIG.3 Daily dicarboxylic concentrations (ng m⁻³) versus temperature (T°C) and ozone concentrations (µg m⁻³). MI, summer

n-ALKANES and PRIMARY BIOGENIC SOURCE

N-alkanes come from anthropic (combustion) and biogenic (primary biogenic) sources. Anthropogenic n-alkanes concentrations are higher than biogenic ones (wax n-alkanes) in all sites (urban, rural and remote sites) (Tab.3). Contribution of biogenic source is higher during summer, with a % of biogenic source to total n-alkanes concentrations (% WNA = %wax N-alkanes) of 10-17%.

	URBAN SITE (MI)		RURAL SITE (OB)		REMOTE SITE (ASC)	
	SUMMER	WINTER	SUMMER	WINTER	SUMMER	WINTER
CPI	1.5 (± 0.1)	1.1 (± 0.1)	1.3 (± 0.1)	1.0 (± 0.1)	1.3 (± 0.3)	1.0 (± 0.0)
% WNA (C20-C32)	17.4 (± 4.6)	4.5 (± 4.9)	11.3 (± 3.5)	1.9 (± 3.4)	10.1 (± 9.5)	0.0 (± 2.2)
ANTHROPOGENIC C20-C32 (ng m ⁻³)	6.0 (± 1.5)	172.6 (± 135.7)	8.2 (± 2.9)	60.7 (± 21.9)	5.3 (± 1.8)	7.5 (± 3.0)
WAX20-C32 (ng m ⁻³)	1.3 (± 0.6)	5.2 (± 4.9)	1.1 (± 0.5)	1.7 (± 2.2)	0.5 (± 0.4)	0.0 (± 0.3)

TABLE 3 N-alkanes C20-C32. Carbon preference index (CPI), % contribution of plant wax n-alkanes (% WNA), anthropogenic n-alkanes concentrations (ANTHROPOGENIC C20-C32) and biogenic n-alkanes concentrations (WAX C20-C32).

N-alkanes were used to estimate total contribution of primary biogenic source (plant debris) to total PM_{2.5} concentrations (Kotianová, 2008). Primary biogenic source is maximum during the leaf falling season (autumn) (1.2-1.4%), and < 1% during other seasons (Fig.4).

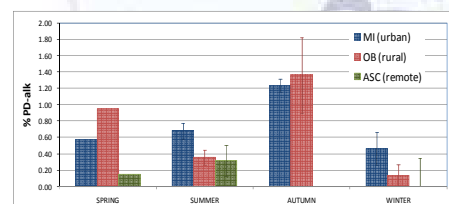


FIG.4 Plant Debris as a % of PM_{2.5} n-alkanes (%PD-alk)

References

- Kotianová P. et al., 2008. "Temporal patterns of n-alkanes at traffic exposed and suburban sites in Vienna." *Atm. Env.*, 42, 2993-3005
- Legrand M. et al., 2007. "Origin of C2-C5 dicarboxylic acids in the European atmosphere inferred from year-round aerosol study conducted at a west-east transect." *J. Geophys. Res.*, 112, D23S07, doi:10.1029/2006JD008019