

Identification of secondary inorganic and organic aerosol components in urban particulate matter samples

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Atmospheric aerosols in urban areas contain a significant fraction of both carbonaceous material and inorganic ions such as nitrate, ammonium and sulphate. Most of these pollutants are of secondary origin. Organic carbon (OC) can be emitted directly into the air or formed in the atmosphere through chemical reactions of reactive organic gases and subsequent gas-to-particle conversion (Secondary Organic Aerosol, SOA). In the present study PM10 samples collected in Milan during a wintertime and a summertime campaign, with a 4-hours time resolution, have been chemically characterized.

Secondary organic carbon can be estimated by subtracting the expected primary OC from the total observed ambient OC. Primary OC can be estimated using different approaches (Turpin et al., 1995; Plaza et al., 2006; Salma et al., 2004; Strader et al., 1999):

$$OC_{\text{prim}} = (OC/EC)_{\text{prim}} EC$$

or: $OC_{\text{prim}} = a + bEC$

where a and b are the intercept and the slope, respectively, of the best fit line. The intercept a is considered to be the primary OC background concentration originating from non-combustion sources. It is supposed that primary OC and EC have the same source, and therefore there is a representative OC/EC ratio for the primary aerosol (EC is only primary in origin). Since $(OC/EC)_{\text{prim}}$ emission rates vary by source (vehicles, fireplaces, heating, etc.) and are influenced by meteorological conditions, it is mandatory to estimate a local and seasonal value for the ratio. These values can be calculated when SOA is expected to be low (low local photochemical activity, i.e. low O_3 concentration and high values for NO_2/NO_x ratio).

In this study six different criteria, some of which already used in the literature, have been employed to estimate $(OC/EC)_{\text{prim}}$. It represents the slope of the linear regressions obtained: (1) choosing the interval time 4-8 a.m. (low photochemical activity and, during summer, traffic as the only active source); (2) low values for NO_2/NO_x ratio; (3) low SO_4^{2-} concentrations; (4) low values for OC/EC; (5) low values of both SO_4^{2-} and OC/EC; (6) low SO_4^{2-} and $C_2O_4^{2-}$ concentrations. It is worth noting that both sulphate and oxalate are typically secondary components deriving respectively from SO_2 and VOCs oxidations.

Depending on the criteria OC_{sec} resulted to vary during the hot and the cold season as shown in table1.

	$OC_{\text{sec}}/OC_{\text{tot}}$ (%)	OC_{sec}/PM (%)
Summer	15 – 40	3 – 9
Winter	20 – 30	5 – 7

Table1: OC_{sec} concentration range

During summer, when O_x ($O_x=O_3+NO_2$) concentrations are higher, a fair agreement with OC_{sec} concentrations has been observed (figure 1).

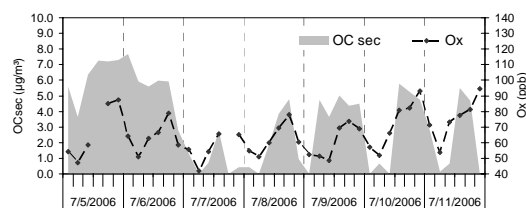


Figure 1: O_x and OC_{sec} concentrations during summer

Comparing the hot and the warm season NO_3^- was higher in winter because of the low temperatures which favor ammonium nitrate formation while during summer it is partially loosened for volatilization. SO_4^{2-} is higher in summer because of the photochemical activity (figure 2).

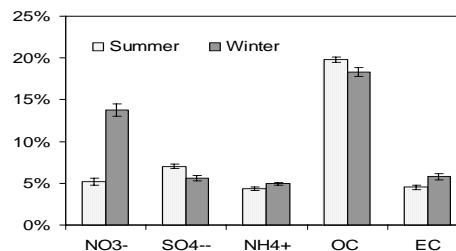


Figure 2 – principal ionic components, OC and EC concentrations in summer and winter

Plaza J. et al. (2006). *Atmos. Environ.*, 40, 1134-1147.

Salma I. et al. (2004). *Atmos. Environ.*, 38, 27-36

Strader R. et al. (1999). *Atmos. Environ.*, 33, 4849-4863

Turpin, B. J. et al. (1995). *Atmos. Environ.*, 29, 3527-3544.