

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

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## Introduction

Elevated particulate matter concentrations in urban areas result not only from direct particulate emission but also from gas-to-particle conversion in the atmosphere. Although carbonaceous species account for a large fraction of aerosol mass, the relative contribution of primary and secondary organic components is still under discussion. A variety of approaches have been used to estimate the magnitude of secondary organic aerosol formation in the atmosphere; this evaluation is difficult and not straightforward because of the large number of organic compounds involved.

In this study 4-hours time resolution PM10 samples (180 in total) collected in Milan during two field campaigns, performed during winter and summer 2006, have been chemically characterised. OC and EC have been determined by means of a Thermal Optical Transmittance Sunset analyser. The data have been used to evaluate Secondary Organic Carbon (SOC) with two different approaches.

The SOC estimation is based on the  $(OC/EC)_{pri}$  ratio, the key point is the accuracy and significance of this ratio in relation to the mixture of local primary PM sources. This method known as EC tracer method, is the most used in the literature.

A comparison of the SOC estimation is performed using Positive Matrix Factorization. PMF is an advanced factor analysis technique computing a weighted, non-negative constrained least squares fit. It imposes non-negativity constraints to the factors and uses realistic error estimates from data standard deviations, as described in Paatero (1997). Sources have been resolved by PMF and the source apportionment has been obtained by Multi Linear Regression analysis. SOC is subsequently taken to be the sum of OC in the sources of secondary nature.

## EC tracer method

OC/EC measured ratios, during summer, shows the same temporal behaviour of the wind velocity (see Figure 1). To estimate primary OC/EC ratio we have selected samples characterised by a low wind velocity. In particular we have selected the data with: low OC/EC ratio ( $OC/EC < 3$ ), high concentration of NO and O<sub>x</sub>, low percentage of sulphate and oxalate (not shown here). The high-time resolution data allowed the identification of samples without SOC, which might be very difficult to detect on 24-hours samples. In this way a robust value for  $(OC/EC)_{pri}$  can be obtained. In Figure 2 the linear regression obtained by the selected OC and EC values is shown.

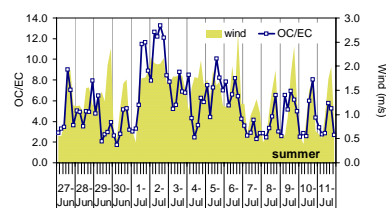


Figure 1

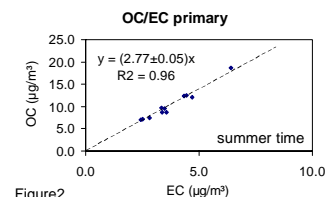


Figure 2

Since the regression line has no intercept, it suggests that background OC (non-combustion OC or biogenic OC) is likely not produced in the urban area but mainly advected by the wind.

Considering all the above listed criteria, it is possible to separate our summer data-set in three categories characterised by different values of the OC/EC ratio as represented in Figure 3.

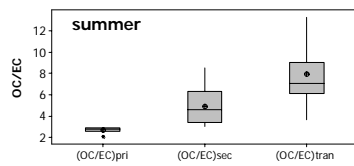


Figure 3

To calculate primary OC we have used the following equation:

$$OC_{pri} = 2.77 \times EC$$

To calculate transported OC we used 5.45 as a multiplicative factor for EC. This value is the 75<sup>th</sup> percentile of  $(OC/EC)_{sec}$  (wind velocity < 1.7m/s,  $OC/EC > 3$ ) data distribution (see Figure 3):

$$OC_{tran} = 5.45 \times EC$$

Secondary OC is calculated as follows ( $OC_{tot}$  is the measured OC):

$$OC_{sec} = OC_{tot} - (OC_{pri} + OC_{tran})$$

The results are represented in Figure 4.

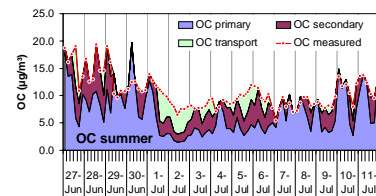


Figure 4

According to our criteria, in Milan during the summer season  $OC_{pri}$  is on average 64% of the total OC. If present,  $OC_{sec}$  and  $OC_{tran}$  are 34% and 31%, respectively, depending on meteorological conditions.

It is noteworthy that the percentage of sulphate, ammonium and oxalate increase during days characterised by the presence of secondary or transported organic carbon.

For the wintertime data set we cannot use a wind velocity criteria, thus we have selected a period characterised by a low and constant OC/EC ratio, as highlighted in Figure 5. In the selected period secondary compounds (i.e. nitrate, ammonium and sulphate) percentages are low and the correlation between OC and EC is very good (Figure 6).

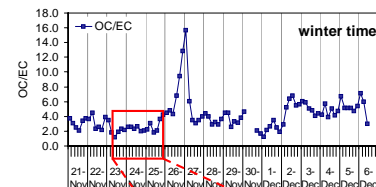


Figure 5

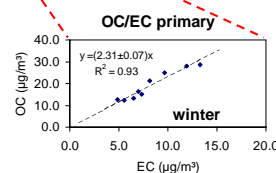


Figure 6

Also for the winter season data-set, the regression line intercept is zero. Furthermore OC/EC ratio is smaller than the summer time one. This result suggests that also in this case the background OC, if present, is not produced in the urban area. OC/EC ratio higher than 5.45 is again an indication of the presence of  $OC_{tran}$ . Primary, secondary and transported OC winter concentrations are reported in figure 7.

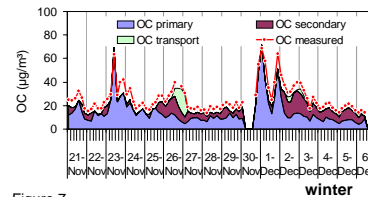


Figure 7

In Milan during wintertime  $OC_{pri}$  is on average 71% of the total OC, while the  $OC_{sec}$  and  $OC_{tran}$  are, if present, 38% and 20%, respectively.

In the two seasons the secondary compounds ( $OC_{secondary}$ : nitrate, sulphate, and ammonium) on PM account as shown in Table 1:

|   | Summer season | Winter season |
|---|---------------|---------------|
| Secondary aerosol (nitrate+sulfate +secondary organic carbon) | 21%±7%        | 30%±11%       |
| Secondary aerosol + transported aerosol                       | 33%±20%       | 34%±17%       |

Table 1

Receptor models estimate the amount of pollutants from different sources through statistical interpretation of ambient data and reasonably imposed constraints. The source categories were identified by the explained variation in species apportioned in the individual sources as well as the temporal and spatial variation of sources contribution. OC concentrations in the three secondary aerosol source categories, i.e. secondary sulphate, secondary nitrate, and secondary organic aerosol, were summed up to obtain SOC.

In both season average SOC percentages obtained by the two methods are comparable (Table 2). Nevertheless, PMF gives a higher value in winter.

In Figure 8 we show a comparison between the two concentration patterns obtained by EC tracer method and PMF method.

|        | EC tracer method | PMF model |
|--------|------------------|-----------|
| Summer | 31%              | 28%       |
| Winter | 38%              | 46%       |

Table 2

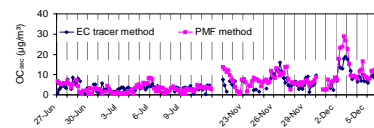


Figure 8

## Conclusions

According to many authors (Strader et al., 1999; Yu et al., 2004) one of the major problems with EC tracer method is that  $(OC/EC)_{pri}$  ratio could not be constant at a site but can vary with sources and meteorological conditions. Although the values used in this study for summertime and wintertime (2.77 and 2.31, respectively) are statistically robust, the SOC concentrations estimated remain partly uncertain.

Another critical point to be taken into account is related to sampling artifacts. Our measurements might have also been affected by these problems.

### References

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