



## Chemical composition and molecular markers for source estimation of PM<sub>2.5</sub> from North of Italy

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PM<sub>2.5</sub> was collected at three locations of the North of Italy: an urban (Milan, MI), a rural (Oasi Le Bine, OB), and an high altitude remote (Alpe San Colombano, ASC, m.2280 asl on Alps) site over 2007/2009. PM samples were analysed for main chemical composition (OC, EC, inorganic ions, elements) and organic molecular markers (n-alkanes C<sub>20</sub>-C<sub>32</sub>, C<sub>2</sub>-C<sub>5</sub> mono and dicarboxylic acids, levoglucosan and PAHs). In MI and OB, carboxylic acids concentrations were in the range of 216-405 ng m<sup>-3</sup>, with no relevant seasonal trend. Otherwise, all the other trace organics (PAHs, n-alkanes and levoglucosan) experienced a strong seasonal trend in the two sites from the plain, with maximum atmospheric concentrations in winter months. At the remote site ASC, trace organic concentrations were very low in all seasons, except carboxylic acids which showed higher summer concentrations, 178 (± 76) ng m<sup>-3</sup>.

A source apportionment study was conducted by CMB model (CMB8.2, EPA). Eight sources have been identified that contribute to PM, including: ammonium sulphate, ammonium nitrate, traffic, biomass burning, natural gas combustion, vegetation debris, dust/soil and salt. PM<sub>2.5</sub> mass at the urban MI and the rural OB sites was quite well represented by those source components, which contributed 61-89%, while only 23% and 50% of PM<sub>2.5</sub> concentrations at the remote ASC site were apportioned respectively in spring and summer. At ASC, the component "other OC" (given by the difference between the measured organic carbon and the sum of all known source contribution estimates obtained from CMB model) was 1.7 [U+F06D] g m<sup>-3</sup> and 0.65 [U+F06D] g m<sup>-3</sup> respectively in spring and summer, representing an high % of ambient OC concentrations (84% and 63%).

Source contributions to individual trace organic species obtained from elaboration on singular molecular marker data were compared with CMB results. PAHs-to-EC ratio-ratio plots, calculated as proposed by Robinson (Robinson et al, 2006 indicated as high molecular weight PAHs (IcdP and BghiP) arose mainly from biomass burning during winter. It was confirmed by CMB model, quantifying winter biomass burning source contributions to IcdP and BghiP concentrations equal to 77-79% in MI, 97-98% OB, and 91-97% at ASC, while in the same period lighter PAHs (BbF and BkF) were quite exclusively attributed to natural gas combustion. n-alkanes C<sub>20</sub>-C<sub>32</sub> had different major contributing sources according C carbon number of n-alkanes, season and sampling site. The percentage of all n-alkanes C<sub>20</sub>-C<sub>32</sub> concentration derived from plant debris was estimated by the experimental index WNA% (Simoneit B.R.T., 1989). Values were maximum during fall season (C<sub>20</sub>-C<sub>32</sub> WNA% = 10%-15%), and from CMB model it was estimated, for the same period, a plant debris source contribution as high as 50-100% for higher n-alkanes C<sub>27</sub>-C<sub>32</sub>.

A very low percentage of carboxylic acid concentrations were apportioned from primary sources. From traffic and biomass source profiles, it has been estimated that less than 3% of oxalic acid concentrations (the carboxylic acid with highest ambient concentrations) were from primary sources in summer, and just a bit higher percentage in winter (summer: MI:3%; OB:2%; ASC:1%; winter: 16%; OB: 8%; ASC =2%).

### Bibliography

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