



Source identification of oxidized organic aerosols in the continental boundary layer and in the free troposphere by nuclear magnetic resonance (NMR) spectroscopic techniques.

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The employ of spectroscopic techniques, such as proton nuclear magnetic resonance (H-NMR) spectroscopy, can be a suitable alternative to molecular tracer analysis for source apportionment of atmospheric organic aerosols. The comparison of HNMR functional group compositions obtained from different areas of the world characterized by different emission types and pollution levels has highlighted that characteristic H-NMR fingerprints can be derived for three major aerosol sources: biomass burning, secondary formation from anthropogenic and biogenic VOCs, and emission from the ocean. Biomass burning particles show the highest content of hydroxyl units while SOA are characterized by the highest carbonyls/carboxyls content. Marine particles contain the lowest amount of both oxygenated groups. Such characteristic functional group compositions are defined as broad ranges and show dependence with the photochemical age of the aerosol. In the Po Valley (Italy), for example, the carbonyl/carboxyl content of SOA is higher in the summer than in autumn/winter on average. Even lower carbonyl/carboxyl amounts are found at a mountain top in north Apennines in winter, when free tropospheric air masses are advected by the Arctic regions. Overall, the functional group composition of organic aerosol samples collected in northern Italy shows a remarkable variability both in the boundary layer and in the free troposphere. In particular, the analysis of selected samples by an innovative

derivatization-NMR technique, allowing for separation between carbonyls and carboxyls units, highlights significant day-to-day variations in the oxidation state of the organic fraction of the aerosol, apparently depending on the photochemical activity. Our analysis shows that H-NMR spectroscopy can profitably be used as a valuable tool for aerosol source identification. Moreover, compared to other existing methodologies, it is able to relate the source fingerprints to integral chemical properties of the organic mixtures, which can be linked to the reactivity and physico-chemical properties of the organic particles in the atmosphere.