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Origin of nitrocatechols and alkylated-nitrocatechols in atmospheric aerosol particles

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Biomass burning constitutes one of the major sources of aerosol particles in most of the environments during winter. If a lot of information is available in the literature on the primary fraction of biomass burning aerosol particles, almost nothing is known regarding the formation of Secondary Organic Aerosol (SOA) from the chemical mixture emitted by this source. Recently methylated nitrocatechol have been identified in atmospheric particles collected in winter. These compounds are strongly associated with biomass burning tracers such as levoglucosan and are suspected to be of secondary origin since they can be formed through the oxidation of cresol significantly emitted by biomass burning. However, nitrocatechols are particularly difficult to analyze using classical techniques like HPLC-MS or GC-MS. In the present study, we adopt a new analytical approach.
Direct analysis in real time (DART), introduced by Cody et al. (2005), allows direct analysis of gases, liquids, solids and materials on surfaces. Thus, for particles collected onto filters, the sample preparation step is simplified as much as possible, avoiding losses and reducing to the minimum the analytical procedure time. Two analytic modes can be used. In positive mode, [MH]+ ions are formed by proton transfer reaction ; whereas in negative ionization mode, [MH]-, M- and [MO_2]- ions are formed. DART source enables soft ionization and produces simple mass spectra suitable for analysis of complex matrices, like organic aerosol, in only a few seconds. For this study, the DART source was coupled to a Q-ToF mass spectrometer (Synapt G2 HDMS, Waters), with a mass resolution up to 40 000.
The analysis of atmospheric aerosol samples, collected in Marseille during winter 2011 (APICE project), with the DART/Q-ToF approach highlighted the abundance of nitrocatechols and alkylated nitrocatechols. Their temporal trends were also very similar to those of levoglucosan or dihydroabietic acid well known tracers of biomass burning aerosol. If their biomass burning origin's is clearly established, their secondary origin remains still not totally clear.
Smog chamber experiments were then conducted in the PSI facilities to investigate the aging of biomass burning emissions. The analysis of samples collected during these experiments using the DART/Q-ToF approach, confirmed that nitrocatechols and methylated nitrocatechols originate from biomass burning processes. More importantly our results confirm that nitrocatechols and their methylated derivatives are quasi exclusively from secondary origin. Considering the abundance of biomass burning primary aerosol, and the large fraction of unexplained SOA, this result is of prime importance.

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