Secondary organic aerosol formation through aqueous phase photooxidation of aromatic compounds

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Secondary organic aerosol (SOA) formed through the gas-phase oxidation of volatile organic compounds (VOCs) and further gas-to-particle partitioning cannot explain the gap between atmospheric observations and model predictions of organic aerosols (Heald et al., 2005). However, there is growing evidence that reactions in atmospheric waters may represent an additional and important source of SOA (Lim et al., 2010). Formation of low-volatility products in the aqueous phase has been observed during reactions of carbonyl and monoaromatic compounds found in the atmosphere (Ervens et al., 2011; Sun et al., 2010).

Monoaromatic compounds can be considered as a proxy for anthropogenic and biomass burning emissions. Methyl-nitrocatechols have been identified as an important class of SOA compounds from biomass burning and proposed as suitable tracers (Iinuma et al., 2010; Kitanovski et al., 2012). In addition to nitrocatechols, other nitro-aromatics were determined in urban winter aerosols (Fig. 1), and constitute nearly 1% of the organic carbon (Kitanovski et al., 2012). A noticeable unknown peak consistent with a nitroguaiacol isomer was also detected in the latter study.

In the present study, the formation of SOA through aqueous-phase photooxidation and nitration of guaiacol (2-methoxyphenol), known to be emitted upon biomass burning, was studied. The main objectives were to chemical characterize the low-volatility products and examine their possible presence in ambient aerosols.

The aqueous phase reactions were performed in a thermostated reactor under well-defined experimental conditions. A solution of guaiacol was exposed to simulated sunlight (Xenon lamp, 300 W) in the presence of H2O2 (source of OH radicals) and NO2−. After isolation of the main reaction products by solid-phase extraction (SPE), their chemical structures were elucidated. To this aim, the SPE extract was first subjected to semi-preparative liquid chromatography, after which the main products were fractionated and isolated. Nuclear magnetic resonance spectroscopy (NMR) and liquid chromatography/negative ion electrospray ionization tandem mass spectrometry (LC/(−)ESI-MS/MS) were used for structural elucidation.

The main products of guaiacol photooxidation and nitration are two nitroguaiacols (4-nitroguaiacol, 4NG; and 6-nitroguaiacol, 6NG) and one dinitroguaiacol (4,6-dinitroguaiacol, 4,6DNG). In addition, several minor phenolic oxidation products and oligomers of guaiacol and nitroguaiacol were formed. Using the isolated compounds as standards, several guaiacol products were identified in ambient PM10 from the city of Ljubljana (Slovenia) by means of LC/(−)ESI-MS/MS.

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