Aqueous-phase formation of methylnitrocatechols as important SOA tracers of biomass burning organic aerosols

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Much of the atmospheric organic aerosol is secondary; thus, a special attention in the last years has been devoted to secondary organic aerosols (SOA), their chemical composition, formation mechanisms and atmospheric aging. In addition to the gas-phase pathways, aqueous-phase can also be an important source of SOA (Ervens *et al.*, 2011).

Biomass burning is a significant source of SOA precursors because of the emission of many organic compounds of various volatilities, including methoxyphenols (Grieshop *et al.*, 2009). Semi-volatile aromatics emitted into the atmosphere undergo transformations in the gaseous and/or aqueous phases, leading to products with lower saturation vapor pressures and higher water solubilities (Li *et al.*, 2014). A good precursor candidate for SOA formation is catechol (Ofner et al., 2014), which is also reported as a strong emission pollutant from biomass burning. Further, methylnitrocatechols (MNCs) have been proposed as tracers of secondary biomass burning organic aerosols (BBOA) (Kitanovski et al., 2012).

Our very recent findings based on quantum chemical calculations of favourable pathways of aqueous-phase electrophilic substitution of 3-methylcatechol (3MC) with nitronium ion (NO_2^+) and on a detailed LC/(-)ESI-MS/MS chemical analysis of MNCs in ambient aerosols, revealed the presence of 3-methyl-4-nitrocatechol (3M4NC), besides 3-methyl-5-nitrocatechol (3M5NC), for the first time (Frka et al., 2016). Moreover, in ambient aerosols from urban background site of Ljubljana, Slovenia, three MNCs, were identified, i.e including 4-methyl-5-nitrocatechol (4M5NC), 3M5NC and 3M4NC (Figure 1).

In the present work the kinetics of the aqueous-phase 3MC nitration was investigated under atmospherically relevant conditions. The laboratory experiments were performed in acidic solution, typical for the atmospheric waters (pH 4.5), both, under dark and simulated sunlight conditions in the presence of nitrite added as $NaNO_2$. 3MC and its main nitro-products, i.e., 3M5NC and 3M4NC were followed by use of a high pressure liquid chromatography (HPLC). Preliminary kinetic studies showed a reasonable agreement with the observed ratio of 3M5NC/3M4NC determined in winter ambient aerosols influenced by biomass burning.

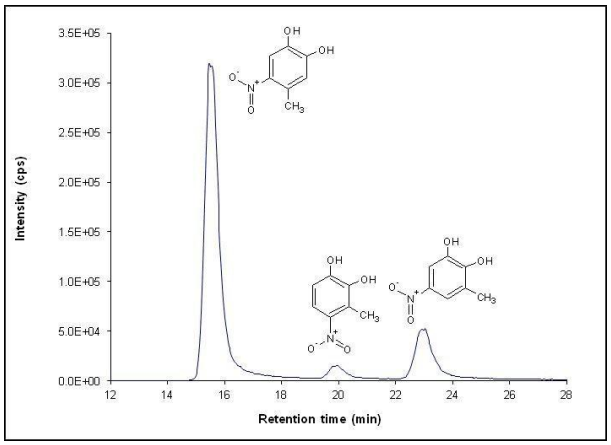

Figure 1. SRM chromatogram for a winter aerosol sample from Ljubljana, Slovenia; 4-methyl-5-nitrocatechol (4M5NC), 3-methyl-4-nitrocatechol (3M4NC) and 3-methyl-5-nitrocatechol (3M5NC).

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