Nitration and oxidation of bioaerosols and allergenic proteins

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Primary biological aerosol particles, e.g. pollen, fungal spores, bacteria, etc., significantly contribute to the coarse mode particulate matter in urban, rural, and pristine environments (Elbert et al., 2007; Després et al., 2012). Up to ~5% of the total urban particulate matter are proteins. These proteins influence the physico-chemical properties of atmospheric particles and play a major role as airborne allergens (Franze et al., 2003)

Protein nitration was found to occur at the tyrosine residues, and to proceed at timescales and NO_2 and O_3 concentrations relevant to the ambient atmosphere (Franze et al., 2005). Moreover, recent studies suggest that nitration affects the allergenicity of proteins (Gruijthuijsen et al., 2006; Untersmayr et al., 2010).

For this study, the reaction products and pathways of protein nitration were investigated using 3 different nitration agents. Nitration of the investigated proteins was carried out in solution using 1) tetranitromethane (TNM), 2) peroxynitrite, and by passing gaseous nitrogen dioxide and ozone (NO_2+O_3) over protein spiked filters as illustrated in Fig 1. The nitration degrees of individual tyrosine residues (ND_Y) were determined by site-specific quantification using HPLC-MS/MS (Zhang et al., 2011) and compared to the total protein nitration degrees (ND) determined by photometric detection with HPLC-DAD (modified Yang et al., 2010).

The observed nitration patterns revealed that the site selectivity of the reaction depends on 1) the nitrating agent, 2) reaction conditions, and 3) molecular structure of the protein. Therefore, different nitration mechanisms in endogenous and exogenous processes lead to specific post-translational modifications of proteins under summer smog conditions in the atmosphere (NO_2 and O_3), or during inflammatory processes in the human body (peroxynitrite). Further, a correlation of ND and relative humidity (RH) was observed for protein nitration by gaseous NO_2 and O_3. Meteorological conditions therefore seem to play an important role in the ambient protein nitration. Atmospheric aerosol samples will be analyzed to investigate the extent of protein nitration and oxidation under ambient conditions.

The chemical mechanisms and molecular processes responsible for the adverse health effects of NO_2 and O_3 are still not well understood. We suggest that protein nitration by air pollutants plays a major role in the increase of allergies in the western countries besides nutrition effects and excessive hygiene practices.

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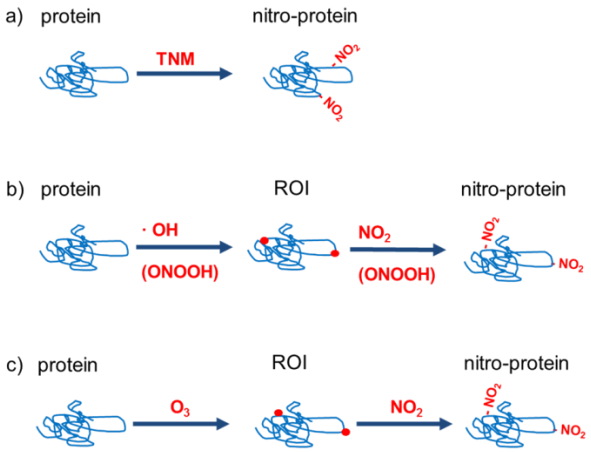

Figure 1: Protein nitration pathways. (modified from Shiraiwa et al., 2012)

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