

# Quantification of stable radicals and reactive oxygen species in atmospheric aerosols by Electron Paramagnetic Resonance spectroscopy

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Ambient particulate matter can cause adverse health effects upon inhalation in the respiratory tract and reactive oxygen species (ROS) and other radicals play a key role in oxidative stress. The chemical mechanism that triggers oxidative stress is still not fully elucidated. Several studies have found that atmospheric aerosol particles contain redox-active components, such as transition metals, which catalyse production of OH radicals by Fenton reactions and interaction with antioxidants in the epithelial lung lining fluid<sup>1</sup>. Moreover, aerosol particles contain stable radicals such as semiquinone radicals. Heterogeneous reaction of O<sub>3</sub> with aerosol particles including polycyclic aromatic hydrocarbons can lead to the formation of long-live reactive oxygen intermediates (ROI)<sup>4</sup>. Upon deposition in the lung lining fluid, such radicals may react with oxygen forming superoxide radical (O<sub>2</sub>)<sup>5</sup> followed by formation of hydrogen peroxide.

At a semi-urban site in Mainz, Germany, ambient particles were collected using a cascade impactor, (MOUDI-II, 122R, MSP), followed by detection and quantification of particle-associated stable radicals and reactive oxygen species using an Electron Paramagnetic Resonance (EPR) spectroscopy. We focus on particles with a diameter smaller than 1 μm, as they can penetrate deeply in the lung efficiently. Organic particles in this size range can be emitted primary upon combustion and formed secondary via oxidation of anthropogenic or biogenic volatile organic compounds followed by condensation of semi- and low volatile oxidation products.

Non-destructive analysis with EPR spectroscopy allowed us to detect stable organic radicals contained in ambient aerosol particles by inserting directly the filter in a high sensitivity cavity. Concentrations of stable radicals in the particle phase were found to be (1 – 7) × 10<sup>11</sup> spin μg<sup>-1</sup> for particles in accumulation mode with diameter of 50 – 500 nm, whereas coarse particles did not contain substantial amounts of stable radicals. Figure 2 shows the temporal evolution of radical concentration in particles within diameters of 100 - 180 nm and 180 – 320 nm collected between 28-05 and 09-06-2015. Maximum values of ~7 × 10<sup>11</sup> spin μg<sup>-1</sup> were reached during sunny days and concentrations as low as 6.3 × 10<sup>11</sup> spin μg<sup>-1</sup> were recorded during rain events, most likely due to particle removal by wet deposition.

Particles were also extracted in ultra-pure water. A variety of radicals formed upon water dissolution were trapped by means of a spin-trapping agent such as 5-tert-Butoxycarbonyl-5-methyl-1-pyrroline-N-oxide (BMPO). The total concentration of radicals trapped is

in the range of 0.1 – 3 × 10<sup>11</sup> spin μg<sup>-1</sup>, with relative amount of OH, carbon-centred and oxygen-centred organic radicals of 25 - 33%, 33 - 65 %, and 10 - 33 %, respectively. We suggest that the formation of such radicals were caused by decomposition of organic hydroperoxides and peroxides (by interacting with quinones) contained in atmospheric organic aerosols.

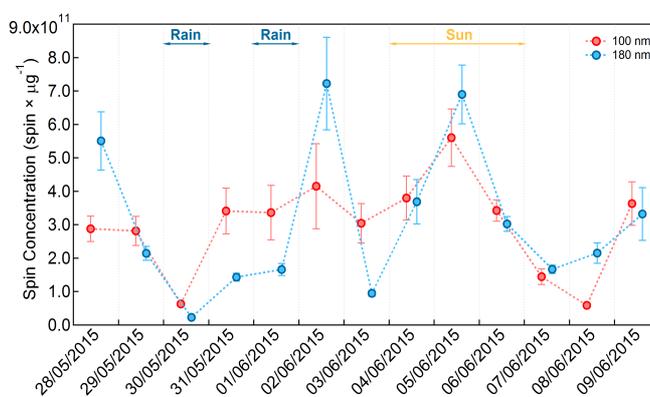


Figure 1. Daily radical concentrations in solid phase particles with diameter of 100 nm (red) and 180 nm (blue), monitored for 13 days.

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