Persistent Free Radicals in Size-Fractionated Aerosols across Climatic Zones: Insights from Subtropical and Temperate Cities

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Abstract

Persistent free radicals (PFRs) are chemically stable yet highly reactive constituents of atmospheric aerosols, capable of generating reactive oxygen species (ROS) and contributing to adverse health effects. This study investigates the concentration levels, size distribution, and diurnal variations of PFRs in $PM_{2.5}$ and PM_{10} aerosols across two contrasting climatic zones: subtropical Tainan, Taiwan, and temperate Moscow, Russia, during late autumn 2023. Ambient aerosols were collected using personal environmental monitors (PEM) in Tainan and a low-volume sampler (PNS 16-3.1) in Moscow. PFRs were quantified via electron spin resonance (ESR) spectroscopy with DMPO spin-trapping. In Tainan, $PM_{2.5}$ PFR concentrations reached $1.22 \times 10^{15} \pm 6.33 \times 10^{14}$ spins/m^3 during the daytime and $1.00 \times 10^{15} \pm 4.17 \times 10^{14}$ spins/m^3 at night, while PM_{10} concentrations were similarly elevated. In contrast, Moscow exhibited significantly lower PFR levels, with $PM_{2.5}$ concentrations of $3.56 \times 10^{14} \pm 1.72 \times 10^{14}$ spins/m^3 (day) and $3.79 \times 10^{14} \pm 2.01 \times 10^{14}$ spins/m^3 (night). When normalized to particulate mass, however, Moscow showed higher PFR content per gram of aerosol. Mass-normalized $PM_{2.5}$ PFRs reached $5.35 \times 10^{19} \pm 4.72 \times 10^{19}$ spins/g-PM during the day and $5.86 \times 10^{19} \pm 4.87 \times 10^{19}$ spins/g-PM at night, exceeding the corresponding values in Tainan. These findings suggest that although ambient concentrations of PFRs are higher in warmer, subtropical environments, aerosols in colder, temperate regions may possess greater oxidative potential per unit mass, likely due to differences in traffic sources and photochemical processing. This study underscores the importance of both absolute and mass-normalized assessments of aerosol-phase radicals in evaluating regional air quality and health risks.

Keywords: Persistent free radicals; Subtropical climate; Temperate climate; $PM_{2.5}$; PM_{10}.