Reactive Oxygen Species Build-up in Photochemically Aged Iron- and Copper-doped Secondary Organic Aerosol Proxy

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The toxicity of particulate matter (PM) is highly linked to the concentration of particle-bound reactive oxygen species (ROS).[1] Chemical properties including metal dissolution and the sources of PM influence ROS production and its oxidative potential.[2,3] Here, the photochemical aging of a secondary organic aerosol proxy (citric acid, CA) with metal complexes (iron citrate) is assessed towards the build-up of particle-bound ROS. The photolysis of the carboxylate complexes initiates free radical chemistry that leads to ROS via the formation of peroxy radicals.[4] Although the photochemistry in viscous iron citrate particles and its effect on degradation and radical persistence has been studied,[5,6] the formation of ROS has not been directly measured so far for this or related systems. Furthermore, we additionally studied the impact of copper on the ROS concentration in the existing iron citrate particle system.

The photolysis of iron/copper citrate particles was experimentally mimicked with an aerosol flow tube in which UV-light irradiation periods and dark periods could be probed. Downstream of the flow tube an online particle-bound ROS instrument (OPROSI), using the acellular assay 2',7'-dichlorofluorescein with horseradish peroxidase continuously quantified ROS.[7] To test different atmospheric conditions influencing the particle's physicochemical properties, the experiments were conducted by combining relative humidity (RH) of 25% or 75%, iron citrate or iron-copper citrate samples, and a nitrogen or air sheath flow used a carrier gases. We found that irradiated CA aerosol containing 10 mole % iron citrate generated ROS concentrations on the order of 0.1 nmol H_2O_2 equivalent μg^{-1}, indicating the photochemically driven formation of peroxides. Increased RH leads to only slight, but overall lower ROS concentration, possibly due to a loss of volatile HO_2 and H_2O_2 into the gas phase in the less viscous particles.[6] The RH effect is enhanced in a nitrogen sheath flow, but in air and compared to the iron citrate particles, the iron-copper citrate samples show a uniformly decreased ROS level. Interestingly, in the high humid, nitrogen experiment with copper, we found a much more pronounced decline of the ROS concentration down to 0.02 nmol H_2O_2 equivalent μg^{-1} compared to all other irradiation experiments. We suggest that copper may suppress radical redox reactions and therefore consume ROS in an anoxic regime.

For the first time, we quantify continuously sampled particle-bound ROS concentrations from an aerosol experiment at different atmospherically relevant conditions. The results prove ROS production from organic aerosol aging processes that adds a natural pathway of enhancing PM toxicity. Assessing the availability of transition metals and their chemical interplay with themselves and with ROS is found to be crucial to exactly determining the oxidative potential of ambient aerosol.

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