Chemical speciation of copper phases in size-fractionated urban ambient particulate matter

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Ambient particulate matter (PM) is the greatest environmental risk to human health with worldwide mortality estimates attributing 4.2 million deaths to ambient PM in 2016 alone. An estimated nine out of ten people globally are adversely impacted by ambient PM; however, disadvantaged communities are often most prominently impacted. Traffic emissions encompass up to 90% of urban ambient PM despite having a global ambient PM contribution of only 7%, which suggests traffic emissions are a more profound contributor to human health impacts than previously recognized. Despite declining exhaust emissions, nonexhaust emissions rich in copper and iron continue to rise. Nonexhaust traffic PM emissions have been identified in cellular studies as having a higher oxidative potential compared to ambient PM. Additionally, several studies of ambient PM suggest copper (Cu) in brake wear is a source of reactive oxygen species (ROS).

While elemental composition and particle size are regularly quantified, few studies have employed synchrotron X-ray spectroscopy to investigate Cu phases in ambient PM. The speciation of Cu in urban ambient PM samples from central and southern California (CA, USA) was investigated using bulk and micro-focused X-ray absorption spectroscopy (XAS). Differences in Cu speciation in two size fractions (PM2.5 and PM0.25) were analyzed. Samples from southern California showed spectroscopic signatures of metallic Cu, while those from central CA exhibited a high fraction of Cu(II) phases. Micro-focused XAS and scanning transmission X-ray microscopy (STXM) analyses also demonstrated Cu enrichment in the finer fraction (PM0.25) suggesting an anthropogenic source. Additionally, bulk and micro-focused XAS results indicate that Cu in urban ambient PM is present in multiple Cu oxidation states, suggesting individual particle chemistry is complex, and that surface chemistry may differ from host phases.