



A detailed analysis of highly time- and size-resolved particle acidity in Pittsburgh and evaluation of acidic particle influence on SOA formation in ambient air

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The mass concentrations and size distributions of non-refractory (NR) chemical species (including SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- , and organics) in submicron particles (approx. PM_{10}) were characterized using an Aerodyne Aerosol Mass Spectrometer (AMS) at the Pittsburgh EPA Supersite from September 6 to 22, 2002 and was part of the Pittsburgh Air Quality Study (PAQS).

Since Pittsburgh particles generally contain very low amounts of the metal ions, such as Na^+ , Ca^{2+} and K^+ , we estimated particle acidity by comparing measured NH_4^+ mass concentration to the predicted amount needed to fully neutralize SO_4^{2-} , NO_3^- and Cl^- . Particles are considered “more acidic” if the measured NH_4^+ concentration is significantly lower than the predicted (when the predicted stoichiometric ratio of bisulfate to sulfate > 1) and as bulk neutralized if the two values are within 10%.

Changes of particle acidity as function of particle size and on highly resolved time grid were investigated. Acidic particles were frequently detected, most often during the high-mass-loading periods, when the size distribution of particles is dominated by the accumulation mode.

In order to evaluate the influence of particle acidity on SOA formation we examined the mass concentrations and size distributions of oxygenated organic aerosol (OOA) vs. particle acidity. OOA concentration and size distribution were estimated using a recently developed custom principal component analysis (PCA) method (Zhang et al, *ES&T*, 39 (13), 4938-4952, 2005). There is strong evidence that the majority of OOA

in Pittsburgh is SOA (Zhang et al., *ACP*, 5, 3289-3311, 2005).

The average mass concentrations and size distributions of OOA were compared between acidic and neutralized periods. The average size distribution during acidic periods is significantly narrower than that during neutralized periods. The average concentrations of OOA during acidic and neutralized periods were 3.28 ± 1.86 and 2.77 ± 1.46 $\mu\text{g m}^{-3}$, respectively. The fact that acidic periods on average contain ~ 0.5 $\mu\text{g m}^{-3}$ more OOA than the neutralized might be the result of SOA photochemical production followed by condensation and/or acid catalyzed SOA formation. Nevertheless, if we attribute the entire difference to acid-catalyzed formation, we can estimate an upper bound of $\sim 18\%$ for the addition of SOA mass to the ambient aerosol due to acid catalyzed SOA formation. This is the first dataset for which such an estimate has been made using ambient data. While this analysis has significant uncertainty due to the comparison of different time periods during a relatively short study, an important result is the lack of very large enhancements of SOA (e.g. several fold, Jang et al. *Science*, 298, 814-817, 2002) due to acid-catalyzed formation.