Comparison of On-line and Off-line methods for the quantification of particle bound Reactive Oxygen Species

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Keywords: SOA, ROS, Instrumentation.
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Aerosol particles have long been associated with adverse health effects in the population. However links between the organic particle fraction and health effects are still poorly understood. It is thought that reactive oxygen species (ROS) present in organic aerosol can cause the observed health effects. There have been many filter collection studies that use adapted biological acellular assays to study the oxidative reactivity of ambient and laboratory generated aerosol. The most popular of which uses the fluorescence probe DCFH due to it's reactivity to a large range of ROS. Due to the reactive nature of ROS efforts have been made to automate the aerosol sampling and analysis process to reduce the time between collection and analysis associated with filter collection, which reduces decomposition of reactive species, and which allows for higher time resolution measurements (Venkatachari and Hopke, 2008). As yet however, there has been no direct comparison between the off-line filter collection methods and on-line automated systems.

In this study on-line and off-line methods were compared by measuring the ROS reactivity of oxidized oleic acid aerosol, a frequently used organic aerosol model system. For online measurements, particles were collected and continuously extracted on a wetted hydrophilic filter (Takeuchi et al., 2005). The particle collector samples air at up to 5 litres per minute and collects particles larger than an aerodynamic diameter of 50 nm with greater than 95% efficiency. The particles are continuously collected and extracted into a solution of horseradish peroxidase (HRP) (0.5 units per ml) that allows immediate reaction of ROS on collection and minimizes any reactive losses of ROS before analysis. The concentration of ROS is characterised following subsequent reaction of the oxidised HRP with DCFH (5 µM) for 10 minutes at 40°C, yielding the fluorescent product DCF in the continuous flow set-up. The concentration of DCF is measured using fluorescence spectroscopy in a flow-through cell and calibrated to ROS concentration with hydrogen peroxide. With a sampling rate of 5 lpm the detection limit of the system is approximately 10 nMoles of hydrogen peroxides per cubic meter of air.

For offline measurements the oxidized oleic acid aerosol particles were collected on a Teflon filter. The filters were collected for a range of times from 1 min to 15 min before extraction in water. The aqueous extract (0.8 ml) was combined with DCFH (1ml, 10 µM, 20 % PBS) and HRP solutions (0.2 ml, 5 units ml^{-1}) and measured with the same fluorescence technique as used in the online measurements.

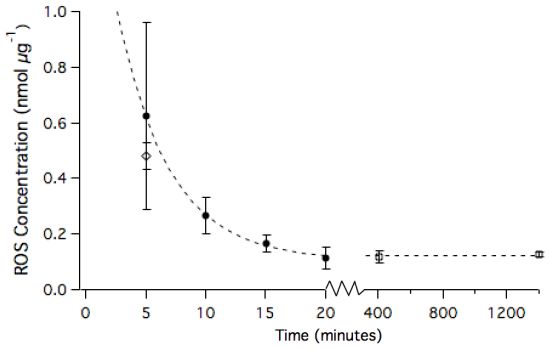

Figure 1. ROS concentration of oxidized oleic acid particles against time between particle collection and analysis. Comparison between online (diamond) and offline (circles) method.

On-line results show a linear relationship between aerosol concentrations and ROS concentrations with a gradient of 0.48 nmol ROS μg^{-1} particle mass. Figure 1 shows the combined results from the online and offline study with the time axis showing the time between start of sample collection and analysis for the offline samples. The ROS concentration determined with the online method is indicated by the open diamond symbol (at 0.48 nmol ROS μg^{-1}). Particles analyzed and collected with the offline method (filled and open circles) showed comparable values only when collected for a very short time (ca. 1min) followed by immediate analysis with ROS concentrations of 0.62 ± 0.33 nmol ROS μg^{-1}. However after a 15-minute delay time between particle collection and analysis the ROS concentration fell by a factor of up to five to 0.12 ± 0.04 nmol ROS μg^{-1}. When the filters were stored in the dark and reanalysed several hours later (open circles), there was no further decrease in the ROS activity (open circles, Figure 1) suggesting the presence of two different types of ROS in the particle.

Thus on-line methods are able to quantify also very short-lived ROS where as off-line studies are not able to capture the most reactive, and potentially the most health-relevant, fraction of particle bound ROS. This study suggests that particle bound ROS off-line studies are likely to greatly underestimate particle bound ROS activity.

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