

Secondary organic aerosol formation from gasoline and diesel vehicle emissions: first results from a new flow reactor

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Vehicle emissions have been shown to significantly impact air quality, especially in urban areas with high traffic flow. Previous studies have mainly concentrated on direct emissions of trace gases and particulate matter (PM) from different types of vehicles. However, recent smog chamber studies have shown that the secondary PM formation from photochemical aging of vehicle emissions dominates the total PM burden. For example, Chirico *et al.* (2010) found a ratio of secondary organic aerosol to primary organic aerosol (SOA/POA) of 1.3–1.7 for a Euro 3 diesel passenger car, and Platt *et al.* (2012) found an even larger SOA/POA ratio (~15.1) for a Euro 5 gasoline car. Nevertheless, relevant studies of SOA formation from vehicle emissions remain very scarce.

Recent studies have demonstrated the utility of flow reactor systems for investigating SOA formation from biogenic, biomass burning and anthropogenic sources (e.g. Cubison *et al.*, 2011; Kang *et al.*, 2011; Saukko *et al.*, 2012). Such reactor systems can provide a highly oxidizing environment that simulates atmospheric oxidation processes on timescales equivalent to one day to several days within a few minutes. Flow systems utilize continuous flow rather than the batch reaction systems employed by smog chambers and therefore provide a faster, time-resolved measurement of the secondary aerosol production potential. Such a fast response is in particular useful for vehicle emission measurements as SOA formation is expected to depend strongly on the engine load.

In this study, the SOA production potential was investigated for gasoline and diesel cars. Vehicle exhaust was sampled into the flow reactor via a constant volume sampler (CVS) system (European Joint Research Centre, Ispra, Italy) during regulatory driving cycles or under steady state conditions. The CVS output was mixed with ozone and water vapour and irradiated with UV light (generating OH radicals, the main atmospheric oxidant) in the flow reactor. OA and nitrate aerosol formed were quantified by a high resolution time-of-flight aerosol mass spectrometer and the gas-phase precursors were quantified using a high resolution time-of-flight proton transfer reaction mass spectrometer. Figure 1 shows an example of the measured mass concentration of organic and inorganic species during a regulatory driving cycle. Also shown are the organic contributions to m/z 43 ($C_2H_3O^+$ and $C_3H_7^+$) and m/z 44 (CO_2^+). The figure

shows time-dependent behavior for both the total mass and chemical composition.

The extent of aging is frequently described in terms of an “OH exposure”, defined as the product of OH concentration and exposure time. The flow reactor used in this study employs a moveable injector, which allows decoupling of these quantities. The effects of OH concentration and aging time on SOA and nitrate formation will be presented.

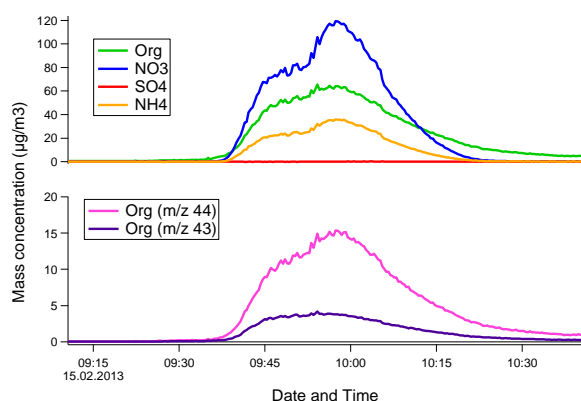


Figure 1. Sample measurements of post-aging particle composition and mass during the regulatory test cycle of a gasoline vehicle.

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