

## On the factors governing the abundance of oxalic acid in tropospheric aerosol particles

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Oxalic acid is frequently observed as one of the most abundant single organic compounds in tropospheric particles. Its sources are commonly believed to be of secondary nature. In state-of-the-art multiphase chemistry models, different pathways exist, which can lead to oxalic acid as final product. Anthropogenic hydrocarbon emissions can be photochemically degraded to glyoxal and methylglyoxal, which – after partitioning into deliquescent particles or cloud droplets – are further oxidized via glyoxylic acid to oxalic acid [Herrmann *et al.*, 2005]. A biogenic oxidation pathway starts with isoprene or monoterpene emissions and leads to glycolaldehyde and methylglyoxal via methacrolein and methylvinylketone, followed by aqueous phase oxalic acid formation [Lim *et al.*, 2005]. As suggested by Warneck, 2003, a marine pathway might exist, starting from marine ethene emissions and leading via glycolaldehyde to oxalic acid.

The aim of this study was to elucidate from field measurements the importance of each of these pathways. To this aim, oxalic acid concentrations from 144 size-resolved particle samples (5-stage Berner impactor) from different continental and coastal European sampling sites were statistically analyzed using principal component analysis (PCA). Hourly back trajectories were calculated for each sampling interval using the HYSPLIT model [Draxler and Rolph, 2003] and combined in a novel way with global land cover data to yield “residence times” of the sampled air masses above urban, agricultural, forested, and oceanic areas. These residence times served as quantitative proxies for different emission regimes (anthropogenic, biogenic, marine) in the statistical analysis. Additionally, meteorological parameters such as sunflux along the trajectories or mixing layer depth at the sampling site were retrieved from the HYSPLIT output.

PCA of the continental dataset retrieved two factors that were connected to the oxalic acid concentrations. A first one showed high loadings on the sunflux as a proxy for photochemical activity together with high loadings on oxalic acid concentrations in all 5 particle size classes. A second factor loads strongly on the air mass residence time above agricultural and urban areas (anthropogenic emissions) and on oxalic acid concentrations in accumulation mode particles (0.42–1.2  $\mu\text{m}$ ). The coastal dataset gave similar results, but included an additional factor with high loadings on oxalic acid concentrations that was not connected to any of the other input parameters. These results indicate that at continental sampling sites the main precursors of oxalic acid are from anthropogenic, rather than biogenic emissions. At coastal sites, though, marine chemistry might be an additional source of particulate oxalic acid.

Draxler, R. R., and G. D. Rolph (2003), HYSPLIT Model access via NOAA website. NOAA Air Resources Laboratory, Silver Spring, MD.

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Warneck, P. (2003), *Atmos. Environ.*, 37, 2423-2427.