EGU21-10743
https://doi.org/10.5194/egusphere-egu21-10743
EGU General Assembly 2021

How quality and quantity of brown carbon influence singlet oxygen production in aqueous organic aerosols

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Singlet oxygen ($^1O_2$) is a reactive oxygen species that has recently gained attention as a competitive oxidant in the atmosphere. This excited state of molecular oxygen is formed by indirect photochemistry in the presence of chromophoric dissolved organic matter (DOM) as sensitizers, molecular oxygen and sunlight. The produced highly reactive intermediate $^1O_2$ is then capable of oxidizing and degrading many organic atmospheric components, thereby affecting their lifetime in the atmosphere. Despite this influence on atmospheric fate, the spatiotemporal distribution of $^1O_2$ in particular matter (PM) is currently unknown. We hypothesized that brown carbon in biomass burning organic aerosols emitted during winter in Switzerland would lead to higher $^1O_2$ steady-state concentrations in PM compared to summer. Therefore, to advance atmospheric $^1O_2$ research, we investigated the $^1O_2$ sensitizing ability of organic aerosols sampled on 24-hour PM10 filters. Specifically, these filters were collected throughout 2013 in Frauenfeld and San Vittore in Switzerland, characterized as urban background and rural traffic measurement stations, respectively. We extracted the water-soluble organic components and quantified $^1O_2$ steady state concentrations as well as $^1O_2$ quantum yield. The quantum yield enhances the data intercomparison as this value shows the normalization of $^1O_2$ production as a function of the rate of absorbance of the organic aerosols. In our ongoing efforts of expanding the spatiotemporal scale of our measurements, our results from Frauenfeld so far show a range between 0.38 – 6.05 · 10^{-13} M for $^1O_2$ steady state concentrations and quantum yields up to 2.1± 0.5%. In preliminary experiments, samples from the rural site San Vittore show similar values, with potentially higher values during periods of significant biomass burning contributions. The values underline $^1O_2$'s potential importance for atmospheric processing, e.g. comparing to Manfrin et al. (ES&T, 2019)[1] who reported $^1O_2$ steady state concentrations of 3 ± 1 · 10^{-14} M from secondary organic aerosols extracts. More importantly, the filter extracts analyzed thus far show a strong seasonal trend, with increased $^1O_2$ values and higher variability in winter as compared to summer. This result corroborates the hypothesis that there is more chromophoric DOM present in winter, due to a higher fraction of brown carbon emitted e.g. in biomass burning for residential heating. To extend this analysis, we are currently correlating the results for $^1O_2$ with molecular markers based on mass spectrometry data available from previous filter analysis provided by Daellenbach et al.,

(ACP, 2017)[2]. Finding these correlations will enable the prediction of $^1O_2$ sensitizing abilities of organic material present in the aerosols both qualitatively and quantitatively. In all, our work will help constrain the seasonal relevance of $^1O_2$ photochemistry in the atmosphere.

References

1. Manfrin, A. et al. Reactive Oxygen Species Production from Secondary Organic Aerosols: The Importance of Singlet Oxygen. Environmental Science & Technology 53, 8553–8562 (2019).
2. Daellenbach, K. R. et al. Long-term chemical analysis and organic aerosol source apportionment at nine sites in central Europe: source identification and uncertainty assessment. Atmospheric Chemistry and Physics 17, 13265–13282 (2017).