

Oxidative Potential of Atmospheric Particles at an Eastern Mediterranean Site

Haroula Baliaka^{1,2}, Despina Paraskevopoulou^{1,3}, Christos Kaltsonoudis¹, Kalliopi Florou¹, Christina Vasilakopoulou^{1,2}, John Kodros¹, Spiro Jorga⁴, Andreas Aktypis^{1,2}, Angeliki Matrali^{1,2}, Mauro Masiol^{1,5}, Spyros N. Pandis^{1,2,4}, and Athanasios Nenes^{1,6}

¹ Institute of Chemical Engineering Sciences, (FORTH/ICE-HT), 26504 Patras, Greece

² Department of Chemical Engineering, University of Patras, 26504 Patras, Greece

³ Institute for Environmental Research and Sustainable Development, National Observatory of Athens, 15236 Athens, Greece

⁴ Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

⁵ Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca' Foscari Venezia, IT-30172 Mestre-Venezia, Italy

⁶ Laboratory of Atmospheric Processes and their Impacts, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Presenting author email: baliaka@iceht.forth.gr

Aerosol oxidative potential (OP; the inherent ability of ambient particles to generate reactive oxygen species *in vivo*) may be linked to the health effects of population exposure to aerosol and is a metric of their toxicity. The goal of this work was to quantify the water-soluble OP of particles in an urban area in Patras, Greece and to investigate its links with source emissions or components of this particulate matter (PM).

A field campaign was conducted during a month-long wintertime period in 2020 (January 10 to February 13) on the campus of the University of Peloponnese in the southwest of Patras. During this time, ambient filter samples (a total of 35 filters) were collected.

To measure the water-soluble OP we used a semi-automated system similar to Fang et al. (2015) based on the dithiothreitol (DTT) assay. The accuracy of our system was validated by measuring the DTT activity of 11 phenanthroquinone (PQN) solutions on both our system and the identical semi-automated validated system at the National Observatory of Athens (NOA). These two sets of analysed DTT activities (current vs. NOA system) were significantly correlated ($R^2=0.99$) with a slope of 1.15 ± 0.04 and an intercept close to zero.

We found that the average water-soluble OP in Patras was $1.5 \pm 0.3 \text{ nmol min}^{-1} \text{ m}^{-3}$, ranging from 0.7 to $2 \text{ nmol min}^{-1} \text{ m}^{-3}$. The OP measured in Patras during the campaign is higher than reported values from similar wintertime studies in other urban areas such as Athens (Paraskevopoulou et al., 2019). The average water-soluble OP during a summer study for Patras was significantly lower and equal to $0.18 \pm 0.02 \text{ nmol min}^{-1} \text{ m}^{-3}$. Taking into account the average PM_{10} mass concentrations for these two periods (summer: $6 \mu\text{g m}^{-3}$ and winter: $23 \mu\text{g m}^{-3}$) it is clear that the increase in OP was two times the increase in PM mass making the wintertime aerosol more toxic.

Additionally, the water-soluble brown carbon (BrC) was determined using an offline semi-automated system, where absorption was measured over a 1 m path length. The average BrC absorption in Patras at a wavelength of 365 nm was $8.6 \pm 3.9 \text{ Mm}^{-1}$ suggesting that there was significant BrC in the organic aerosol during this period.

The coefficients of determination, R^2 , in Table 1 are used as a metric of the potential relationships between the various carbonaceous aerosol components and the DTT activity. The results suggest that the OP is not dominated by a single source or component, but that there are multiple components contributing to it during the study period.

Table 1. Correlation coefficients (R^2) between the water soluble DTT activity of fine aerosol and chemical species

| Carbonaceous Aerosol Component | R^2 |
|--------------------------------|-------|
| Brown Carbon | 0.46 |
| Black Carbon | 0.36 |
| Traffic – related OA | 0.35 |
| Cooking- related OA | 0.32 |
| Oxygenated OA | 0.31 |
| Biomass burning OA | 0.28 |

Interestingly, the highest correlation coefficient ($R^2 = 0.46$) was found between the OP and Brown Carbon. This is consistent with recently published results for an urban site in Atlanta where the oxidative potential measured with the DTT method also had stronger correlations with BrC during the winter (Gao et al., 2020).

References

- Fang, T., V. Verma, H. Guo, L. E. King, E. S. Edgerton, and R. J. Weber. "A semi-automated system for quantifying the oxidative potential of ambient particles in aqueous extracts using the dithiothreitol (DTT) assay: results from the Southeastern Center for Air Pollution and Epidemiology (SCAPE)." *Atmospheric Measurement Techniques* 8, no. 1 (2015): 471-482.
- Paraskevopoulou, D., A. Bougiatioti, I. Stavroulas, T. Fang, M. Lianou, E. Liakakou, E. Gerasopoulos, R. Weber, A. Nenes, and N. Mihalopoulos. "Yearlong variability of oxidative potential of particulate matter in an urban Mediterranean environment." *Atmospheric Environment* 206 (2019): 183-196.
- Gao, Dong, Krystal J. Godri Pollitt, James A. Mulholland, Armistead G. Russell, and Rodney J. Weber. "Characterization and comparison of PM 2.5 oxidative potential assessed by two acellular assays." *Atmospheric Chemistry and Physics* 20, no. 9 (2020): 5197-5210.