

# Evaluating the toxicity of airborne particulate by measuring oxidative potential with spectrophotometric a-cellular assays

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An emerging hypothesis of the mechanism of adverse effects of PM exposure to humans health is that it is mediated by inflammatory responses originating from PM-induced oxidative activity, leading to the generation of reactive oxygen species (ROS). For assessment of the capacity of a PM sample to generate ROS, the oxidative potential (OP) has been proposed, as a biologically more relevant metric than PM mass.

Given the different assays developed for measuring OP, the primary goal of this study was to compare two common a-cellular assays in order to highlight their sensitivity to the ROS generating compounds. One assay measures the consumption of dithiothreitol (DTT) based on the ability of redox active compounds to transfer electrons from DTT to oxygen,  $OP_{DTT}$  (Charrier and Anastasio, 2012). The other common assay is based on the ability of PM to deplete antioxidants such as ascorbic acid,  $OP_{AA}$  (Zielinski *et al.*, 1999).

The performances of the two assays were investigated with standard solutions of individual redox-active species that are common in ambient PM, such as quinones and transition metals. Quinones – mainly phenanthrenequinone and 1,2-naphthoquinone – were found more efficient at oxidizing DTT compared to the less reactive transition metals, i.e., copper, manganese, nickel, chromium, iron. On the contrary, the AA assay is more sensitive to transition metals – mainly copper, chromium, iron and nickel – in comparison to quinones. Both methods were applied to real-world urban  $PM_{2.5}$  samples collected in the Bologna area (Northern Italy) in winter and summer. The obtained data are not correlated, as revealed by comparing the values of each assay, using Pearson correlation coefficient ( $r \sim 0.1$ ).

To give insight into the contribution of PM chemical composition on OP, the assay responses have been expressed on mass basis per  $\mu\text{g}$ ,  $OP_{DTT\mu\text{g}^{-1}}$  and  $OP_{AA\mu\text{g}^{-1}}$  (Figure 1). For both the assays, the computed values are significantly lower (significance t test at  $p < 0.05$ ) for the two filters collected during wintertime (more loaded  $PM_{2.5}$  filters). This may be explained by the larger contribution of photochemical aging and secondary processing during the warmer seasons, that enhance redox activity of the ambient aerosols (Saffari, *et al.*, 2015).

The relationship between the oxidative potential and  $PM_{2.5}$  mass show largely different behaviour of the two assays. In fact,  $OP_{DTT}$  response shows a high correlation with  $PM_{2.5}$  mass (Pearson's  $R > 0.97$ ), indicating linear increase of oxidative activity with  $PM_{2.5}$  mass, while the  $OP_{AA}$  values were not correlated with  $PM_{2.5}$  (Pearson's  $R < 0.05$ ), suggesting that this metric

may be considered an intensive property of PM related to its composition more than to its amount.

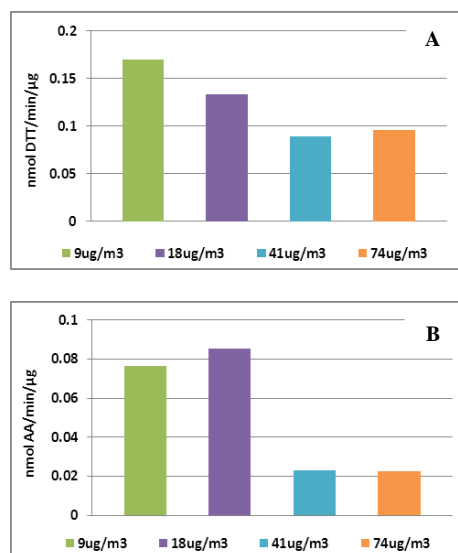


Figure 1. Response of DTT (A) and AA assays (B) expressed on  $PM_{2.5}$  mass basis measured on real samples. Green and purple bars: filters collected in summertime; blue and orange bars: filters collected in wintertime.

In order to highlight the role of the species that mostly contribute to OP, some of the studied samples were submitted to atomic absorption spectroscopy analysis for determining the concentrations of water-soluble transition metals commonly present in ambient PM, i.e., Cu, Zn, Cr, Fe, Mn and Ni. The highest correlations with metals concentrations were observed for the  $OP_{AA}$  values, excellent with Fe and moderate with Cu. These findings are in line with the general notion of the different sensitivity of the two OP methods to transition metals. Consequently, the combination of the two approaches can strengthen each other in giving information to assess the role of organic and inorganic species towards ROS generation from ambient particles.

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