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Editorial

Oxidative Potential of Atmospheric Aerosols

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1. Introduction

Atmospheric particulate matter (PM) is one of the leading health risks worldwide [1,2]. Several epidemiological studies have provided evidence of the association between exposure to PM and the onset of cardiovascular and respiratory diseases [3], as well as cardiopulmonary diseases and other adverse health effects [4]. The exact mechanisms leading to PM toxicity are not fully known, however, several studies suggest that the generation of reactive oxygen species (ROS) could be a major mechanism by which PM leads to both chronic and acute adverse health effects [5,6]. For this reason, in recent years, the oxidative potential (OP) of PM, defined as its ability to generate oxidative stress in biological systems, has been proposed as a relevant metric for addressing PM exposure [7,8]. However, the link between OP and adverse health effects is still uncertain [9–11], and contrasting results have been obtained when PM oxidative potential has been compared with the results of in-vivo and in-vitro toxicological tests or the outcomes of epidemiological studies [12].

The OP can be evaluated through several in vitro assays, but protocols employing chemical (acellular) assays have become common as well. Acellular assays can be useful for investigating the PM properties which are responsible for oxidative stress: ROS compounds can either be carried by components of the aerosol itself (particle-bound ROS) or induced by the catalytic activity exerted by aerosol constituents (PM-induced ROS). The diverse OP assays developed so far have certainly improved our knowledge of the mechanisms underlying PM oxidative stress. At the same time, they pose the issue of comparability between the different assays and protocols, as well as problems surrounding the actual correlation between acellular OP and in vitro (or in vivo) toxicity. Measurements of PM oxidative potential are influenced by the chemical composition of the aerosol, by its size distribution, and by the weight of different natural and anthropogenic sources of PM leading to temporal and spatial variabilities that need investigation in current research. Moreover, recent studies show that photochemical aging increases the oxidative potential of atmospheric aerosols. However, several aspects regarding the specific chemical species, aerosol sources, and atmospheric processes that affect OP are not well established, and further research is needed [13–15]. Another topic that needs extensive research is the characterization of the OP of indoor aerosols.

This special issue includes five research papers and two review papers discussing recent advances in the studies of the oxidative potential of atmospheric particulate matter.

2. Recent Advances in the Characterization of PM Oxidative Potential

The review of Jiang et al. [16] discusses the use of a dithiothreitol (DTT) assay to evaluate the OP of atmospheric aerosols, assessing the current challenges and limitations of DTT measurements. Their analysis shows that the DTT assay has the advantage of screening a large number of PM samples within a relatively short amount of time, providing

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initial insights into the oxidative capacities of PM to deplete thiol antioxidants. This correlates well only with the generation of H_2O_2, but not with other types of ROS. Overall, it is essential for future studies to continue elucidating the chemistry behind the DTT assay to improve our understanding of the underlying mechanisms for a more accurate interpretation of OP^{DTT}. Moreover, Jiang et al. [16] discuss the importance of taking into account both PM-bound ROS and PM-induced ROS, as well as their interactions.

The review of Pietrogrande et al. [17] was intended to give a picture of the spatial and seasonal variability of OP data measured across Italy. The work summarized results obtained in 19 studies covering 9 sites using different acellular assays: dithiothreitol (OP^{DTT}), ascorbic acid (OP^{AA}), glutathione (OP^{GSH}), and 2′,7′-dichlorofluorescein (OP^{DCFH}). The DDT assay appeared sensitive to the organic compounds, mainly accumulated in the fine PM fraction, such as tracers of burning sources, and redox active organics associated with other markers of photochemical aging. In contrast, OP^{AA} and OP^{GSH} were responsive to metals, mainly those related to non-exhaust traffic emissions (Cu, Zn, Cr, Fe, Ni, Mn, Sn, Cd, and Pb) that are predominantly present in coarse PM. In addition, a gradient of increasing OP values from sites in southern to northern Italy was observed.

Frezzini et al. [18] proposed an original acellular assay to measure the OP of PM samples based on the application of 2,2-diphenyl-1-picrylhydrazyl (DPPH). The assay, commonly applied to biological matrices, was well adapted to PM, showing good performance in terms of sensitivity and repeatability. Tests were done using samples representing different sources (certified urban dust NIST1648a; brake dust; Saharan dust; coke dust; calcitic soil dust; incinerator dust; and diesel particulate matter certified material NIST1650b), and their preliminary results indicated that the assay gave a linear response and showed detection limits suitable for the amounts of reducing species present in PM samples.

Cesari et al. [19] investigated the approaches used to estimate the contribution of different sources to the oxidative potential of $PM_{2.5}$ in an industrial site in southern Italy. Two approaches of source apportionment were compared: a PMF run including OP^{DTT} in the input variables, and a multi-linear regression (MLR) analysis performed between measured OP^{DTT} and output of the PMF. The two approaches gave similar results, showing a negligible contribution by secondary sulfate to OP^{DTT} and a larger contribution by combustion sources (i.e., biomass burning and road traffic). Major differences were observed for the impacts of crustal and marine sources, which were larger using MLR compared to PMF. In general, the contributions of the different sources to OP^{DTT} and to $PM_{2.5}$ were not correlated because the industrial source showed the smallest contribution to $PM_{2.5}$ but a large contribution to OP^{DTT}. On the contrary, secondary sulfate, which contributed greatly to $PM_{2.5}$, showed a negligible contribution to OP^{DTT}.

Calas et al. [20] investigated the seasonal variation of the OP responses of more than 700 PM_{10} daily samples collected at seven different urban background environments in France. The large dataset was obtained using both ascorbic acid and dithiothreitol assays. A common seasonal variability, with OP activity being higher in wintertime, was observed at all investigated sites. Correlation analysis was used to associate the measured OP responses with the concentrations of some major chemical components of PM_{10} and their OPs. The major components identified as OP predictors were: organic carbon, elemental carbon, monosaccharides, and Cu. These chemical species are typically emitted by road transport and biomass burning, targeting sources that were likely the major contributors to the measured OP activity. Comparison of measurements at the different sites showed that OP is a site- and assay-dependent variable, so that there is a need for the standardization of this parameter if it has to be used for regulatory purposes. For this goal, it would be useful to investigate additional site typologies such as industrial, rural background, and roadside to generalize results and to determine the best OP predictors across Europe.

Manigrasso et al. [21] performed size-segregated aerosol measurements at an urban site (near Roma in central Italy) and at an industrial site (near Ferrara in Northern Italy). The oxidative potential of the PM soluble fractions was assessed by different acellular assays: AA, DTT, and DCFH. Measurements were used to estimate the size resolved distribution

of elements, ions, and OP responses in the head (H), tracheobronchial (TB), and alveolar (Al) regions, using the multiple-path particle dosimetry (MPPD) model. Results showed that the insoluble PM fraction was more abundant in the coarse sizes compared to the fine sizes. Therefore, the percent of the total respiratory dose deposited in TB and Al regions increased for the soluble fraction. The analysis showed that the total respiratory doses due to brake and soil resuspension sources were higher at the urban than at the industrial site. On the other hand, anthropogenic combustion sources gave larger contributions at the industrial site. Even if further studies are needed, Manigrasso et al. [21] suggested that the OP responses from AA assay could be considered appropriate to address the ROS generation of aerosols that mainly deposit in the H region, whereas DTT and DCFH would be more suitable to measure oxidative activity in the TB and Al regions.

Lionetto et al. [22] used DTT assay to measure the OP of the water-soluble fraction of PM_{10} collected at an urban background site in Lecce (southern Italy), and correlated their results with the outcomes of in-vitro and in-vivo toxicological tests. Specifically, the Microtox® test on Vibrio fischeri bacteria was used to assess the ecotoxicological potential, and the in-vitro MTT assay on the human cell line A549 was used to estimate the cytotoxicological potential of PM_{10}. Results indicated that both MTT and Microtox assays showed time-dependent and dose-dependent outcomes. Some PM_{10} samples presented significant ecotoxic and cytotoxic response, but the correlation with PM_{10} concentration was limited, thus suggesting that these biological endpoints depend on PM_{10} chemical composition and not only on exposure concentrations. MTT and Microtox outcomes were not correlated suggesting that the two toxicological indicators are sensitive to different properties of PM. Intrinsic oxidative potential (i.e., OP normalized by PM_{10} mass) was correlated with mortality observed with MTT test; however, it was not correlated with Microtox outcomes.

In summary, this group of articles provides a valuable update on research concerning the oxidative potential of atmospheric aerosols, showing not just how far the research community has come, but how much work we still have to do in this field of research.

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