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CHARACTERIZATION OF THE OXIDATIVE POTENTIAL OF WATER SOLUBLE FRACTION OF ATMOSPHERIC AEROSOL AND ITS CORRELATION WITH CARBON CONCENTRATIONS

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Abstract: This paper describes the evaluation of the oxidative potential of atmospheric aerosol, for the $PM_{2.5}$ and PM_{10} size fractions, using the DTT assay. This is an indicator related with oxidative stress of particulate matter (PM) leading to potential health effects. Measured DTT activity has been correlated with aerosol concentrations and with the content of carbonaceous species on collected samples. The oxidative potential of PM associated to natural sources during Saharan Dust and sea-spray advection events is investigated and compared with non-event days.

Keywords: Oxidative potential, DTT, atmospheric aerosol, organic carbon, elemental carbon.

1. INTRODUCTION

The growing scientific interest in atmospheric particulate matter (PM) is due to its capability to affect both Earth's climate system and human health. Therefore, the management of air pollution is one the most challenging problems, at global level, in environmental sciences. As stated in recent authoritative literature [1, 2], the impact of $PM_{2.5}$ (particles with diameter <2.5 μm) play an effective role on determining the air quality affecting human health potentially causing premature deaths Worldwide. According to their aerodynamic diameter, particles can penetrate deep and deposit in different parts of the human lung resulting in varying degree of toxic effects [3]. In particular fine particles are more dangerous than coarse particulate due to their smaller sizes and higher exposed surface area that becomes available for adsorption of potentially toxic organic species [4]. Several epidemiological studies established the association of adverse effects on human health with ambient particulate pollution and even if the exact mechanisms of toxicity are still poorly understood, various PM characteristics, such as surface area of particles, transition metal content, surface absorbed organic components, and biological products, have been proposed [5, 6].

Reactive oxygen species (ROS) either transported on particles or catalytically generated by particles through redox reactions are suspected to cause injurious cellular responses so that oxidative potential (OP) of PM is considered as an indicator of potential health effects [7, 8]. Among the various assays developed for measuring OP, the spectrophotometric kinetic method based on dithiothreitol (DTT assay) is largely used [9]. This monitors the depletion of DTT (a surrogate for cellular antioxidants) as catalyzed by the redox-active species in PM. Limited analysis of aerosol OP have been performed, up to now, in Italian measurement sites.

This work is focused on the discussion of a methodology to investigate the OP, using the DTT assay, of water soluble $PM_{2.5}$ and PM_{10} collected in an urban background site in Southeastern Italy. The OP values will be correlated with OC and EC concentrations investigating the influence of secondary organic carbon on measured aerosol OP in $PM_{2.5}$ and PM_{10}. Specific events, including high carbon concentrations and Saharan Dust outbreaks (SDOs) were identified. The oxidative potentials during these events were compared with the typical values observed in the study area in order to investigate the differences in potential oxidative stresses of natural and anthropogenic sources of pollution.

In addition, the chemical speciation of the aerosol, made by using the Fourier Transform InfraRed spectroscopy (FTIR), is used for identification and quantification of functional groups in the organic mass of atmospheric aerosol (e.g., aliphatic, carboxylic acids, hydroxyls, amines, carbonyl groups, and aromatic structures) and of main mineral dust components, both water-soluble and insoluble, such as silicates, carbonates, and other widespread inorganic polyatomic ions [10, 11]. FTIR spectroscopy allows quantifying organic matter (OM) by functional groups rather than individual compounds and the main advantage of FTIR is that nearly all of the organic carbon can be detected, thus providing the calculation of OM using the OM-to-OC ratio [11].

2. MATERIALS AND METHODS

Daily $PM_{2.5}$ and PM_{10} samples were collected on quartz substrates (Whatmann, 47 mm in diameter) using a dual channel sampler (SWAM, Fai Instruments) with on-line detection of particulate matter concentrations based on β-ray attenuation [13]. The measurements were taken at the

Environmental-Climate Observatory of Lecce (Figure 1), regional station of the Global Atmosphere Watch network (GAW). The Observatory is located at the ISAC-CNR premises in Lecce (40°20'8''N-18°07'28''E, 37 m asl) and it could be considered an urban background station about 4 km distant from the town of Lecce and between 30 km and 80 km from the large industrial sites of Brindisi and Taranto.

Fig. 1) Photograph of the Environmental-Climate Observatory of ISAC-CNR in Lecce.

A punch (1.0 cm^2) of each filter was used for the determination of organic (OC) and elemental carbon (EC) via thermo-optical method (Sunset OC/EC Analyzer), following the NIOSH-870 protocol. Quartz filters were pre-fired at 700 °C for 2 hours in order to minimize the organic carbon contamination.

One quarter of the filter was used for the determination of the OP of the water soluble content using the DTT (dithiothreitol) assay. Water soluble content was extracted in 15mL of deionized water (DI, Milli-Q; > 18 MΩ) via sonication in a water bath for 30 min. The extracts (WS-$PM_{2.5}$ and WS-PM_{10}) were then filtered using PTFE (polytetrafluoroethylene) 0.45 µm pore syringe filters to remove insoluble materials and residual fibres. In the assay, the samples, relative to known PM masses, were incubated at 37 °C with DTT (100 µM) in 0.1M potassium phosphate buffer at pH 7.4 (5 mL total volume) for times varying from 5 to 90 min. At designated times, 0.5 mL aliquot of incubation mixture was picked up and was added 0.5 mL of 10% trichloroacetic acid for stopping the reaction. Then, this reaction mixture was mixed with 2 mL of 0.4M Tris–HCl, pH 8.9 containing 20mM EDTA and 25 µL of 10mM DTNB. The concentration of the formed 5-mercapto-2-nitrobenzoic acid was measured by its optical density absorption at 412 nm. The rate of DTT consumption (δDTT, pmol/min) was determined from the slope and intercept of linear regression of measured absorbance versus time. Three replicates have been done, for each sample, and the variability (standard deviation) among the replicates was taken as uncertainty of the measured DTT activity. An example, showing the slope, is reported in Figure 2. In several sample it has been observed a non-linear behaviour at times larger than 60 minutes so that evaluation of the slopes was generally performed in the time interval up to 60 minutes.

The final DTT activity could be normalized in terms of sampled volume (DTTv) or in terms of collected aerosol mass (DTTm). The two point of view are not equivalent because the OP is an extensive property meaning that it increases, on average, when the collected mass of aerosol increases. DTTm represents an intrinsic property of particles linked to sources, while DTTv depends on emission rates and dilutions and characterizes the exposition to particles.

The final DTT activity for a sample was calculated by subtracting a blank value from the sample and normalized by particle overall mass represented by the sample in the incubation vial expressed in the units of pmol/min*µg for DTTm activity and as nmol/min*m^3 for DTTv activity.

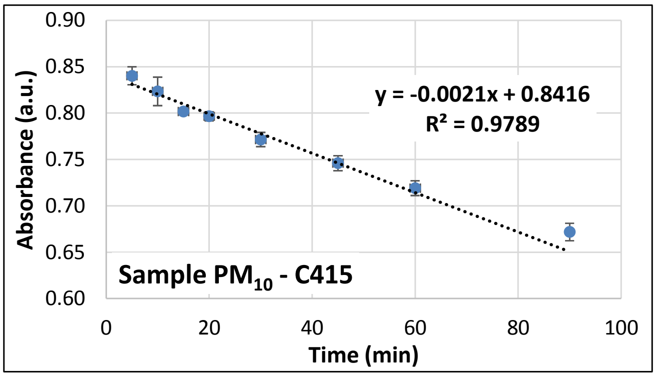

Fig. 2) Example of the linear correlation relationship between absorbance and reaction time.

Mid-infrared spectra of particulate matter were collected using a Perkin Elmer Spectrum One spectrometer equipped with a DTGS detector and a horizontal ATR apparatus (DuraSamplIR). The internal reflection element (IRE) was a three bounce diamond prism 4 mm in diameter. The quartz filter was pressed onto the ATR crystal in order to achieve the efficient adhesion of the particulate matter onto the IRE surface. The resolution was 4 cm^{-1}. 32 interferograms were collected and averaged for each spectrum.

The extraction of the soluble fraction was achieved in a plastic microtube using 1 mL deionized water. A small filter area (0.80 cm^2) was employed. The filter was vortexed with the solvent for 1 min and sonicated for 10 min in ultrasonic bath operating at 35 kHz (Bandelin, Sonorex). Insolubilized material was separated by centrifugation at 7000xg for 4 min using a bench-top microfuge (Hettich, Mikro 120). A 4 uL aliquot of the supernatant was cast onto the ATR prism and dried. The mid-IR spectrum of the resulting dry film was then acquired. An example of acquired mid-infrared spectra of the whole particulate and of the water soluble fraction are shown in Figure 3 for different samples. Some absorption bands have been assigned to main inorganic species and organic functional groups, using model compounds for direct comparison and available data from literature [14]. Figure 3 shows significant differences among the samples and the proposed technique was efficient in putting in evidence these differences helping in identifying the chemical species mainly responsible for the measured OP.

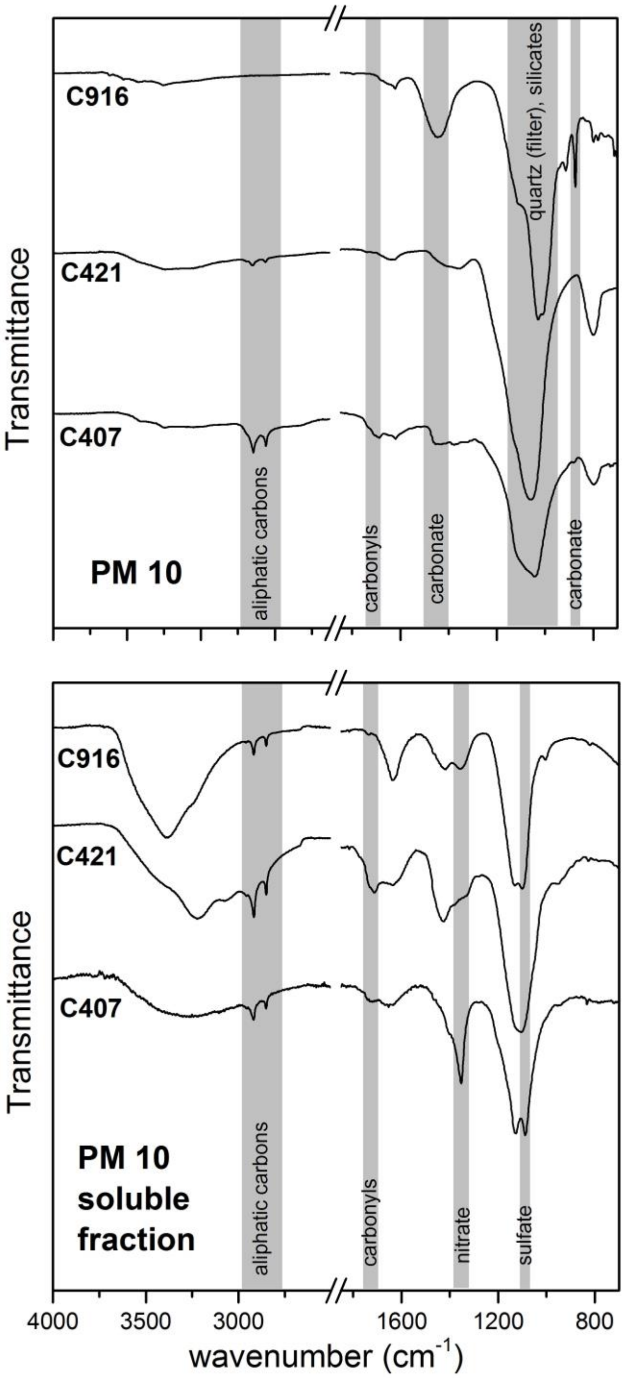

Fig. 3) Example of ATR-FTIR spectra of the whole particulate (top) and of the water soluble fraction (bottom) for three different samples of PM_{10}.

3. RESULTS

The typical yearly average $PM_{2.5}$ and PM_{10} concentrations are reported in Table 1. Table 1 includes also the OC and EC concentrations observed at the site. The ratio $PM_{2.5}/PM_{10}$ is 0.63 (±0.16 standard deviation). This is a ratio typically observed at urban background site in Southern Italy [15].

OC and EC concentrations have a clear seasonal pattern with larger concentrations observed in autumn and winter. A large contribution to OC was given by biomass burning prevalent in winter due to domestic heating, however, relevant also in spring and summer periods because of emissions due to agricultural practices [16]. Both OC and EC are mainly present in the fine ($PM_{2.5}$) fraction. The organic matter (OM) concentrations were estimated as OM = 1.6*[OC], using the coefficient 1.6 for both size fractions [17, 18]. OM accounted for 31% of PM_{10} and 43% of $PM_{2.5}$. The OC/EC minimum ratio method was used to estimate the secondary organic carbon (SOC) concentrations [19] applying the equation:

$$SOC = OC - (OC/EC)_{min} \qquad (1)$$

where the $(OC/EC)_{min}$ ratios were determined graphically looking at the minimum slope of the correlation between OC and EC concentrations. These ratios were 2 for PM_{10} and 1.6 for $PM_{2.5}$. Secondary OC was essentially contained in $PM_{2.5}$ and virtually absent in PM_{10} accounting for 82% of total OC and 22% of $PM_{2.5}$.

Fraction	Concentration µg/m^3	OC µg/m^3	EC µg/m^3
$PM_{2.5}$	18.7 (11.3)	5.0 (4.8)	0.8 (0.7)
PM_{10}	29.5 (19.2)	5.7 (4.9)	0.6 (0.4)

Table 1) Yearly average concentrations and standard deviations (in parenthesis) observed at the site.

Some couples of samples ($PM_{2.5}$ and PM_{10}) have been selected for the determination of the OP using the DTT assay on the water soluble fraction of aerosol. Specifically, the samples considered could be divided into three groups. The first group are samples with OC and EC comparable with the long-term average values; the second group represents cases of high OC and EC concentrations; the third group represents cases of Saharan Dust outbreaks (SDO), quite frequent in the area studied [15]. During SDO events there is a significant increase of PM concentration in the coarse fraction (particles larger than about 2.5 µm) and limited changes in $PM_{2.5}$ concentration [20, 21]. During SDO events it has been observed an increase of marine aerosol content (mainly in the coarse fraction), likely due inclusion of sea-spray during the transport of air masses above the Mediterranean Sea. Data shows an increase of OC concentration in the coarse fraction (2.5 µm < diameter < 10 µm) during SDO events compared to the average OC concentration in this size fraction.

In Figure 4 the measured DTT activity is reported for some selected samples using both normalizations (in volume and in mass). The OP_{DTT} is quite variable from sample to sample and the observed ranges are comparable with the results obtained in other background areas and lower than typical values observed in industrial sites. Observed OP_{DTT} values in this work are comparable with results obtained in other Italian sites. In Bologna (Italy), DTTv of $PM_{2.5}$ (water soluble fraction) were between 0.2 and 1.7 nmol/min*m^3 [22]. Comparable values were also observed in Milan for methanol-soluble total suspended particles [23]. OP_{DTT} values between 0.1 and 0.8 nmol/min*m^3 for $PM_{2.5}$ were observed at different sites in USA during the SCAPE study, with limited differences among the sites with the exclusion of traffic sites that presented larger values of OP_{DTT} [24, 25]. Larger OP at traffic sites than at background sites were also observed in Netherlands during the RAPTES study [26]. The DTTv observed for $PM_{2.5}$ in Los Angeles (USA) ranged between 0.2 and 0.6 nmol/min*m^3 with DTTm between 20 and 45 pmol/min*µg [8].

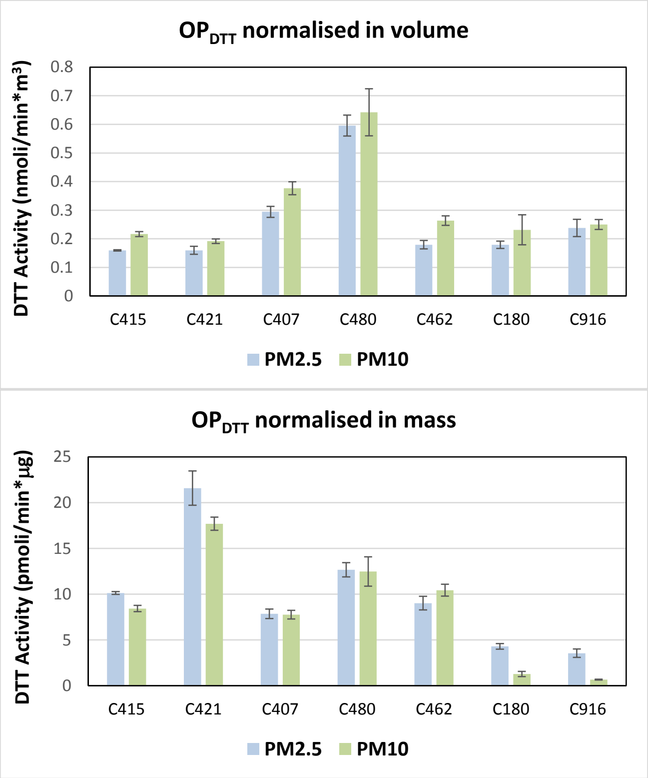

Fig. 4) DTT activity normalized in volume (top) and in mass (bottom) for some selected $PM_{2.5}$ and PM_{10} samples.

In general, it could be observed that DTTm activities are larger on $PM_{2.5}$ than on PM_{10} for typical content of carbonaceous species (samples C415 and C421). This does not happen for the group with high carbon content (samples C407, C480, and C462) in which the OP_{DTT} in the two size fraction is similar. The SDO cases (samples C180 and C916) present a significantly lower OP_{DTT} in both size fractions and the differences of the DTTm activity in the two size fractions are maximized. This is interesting because a significant component of OC was observed in the coarse fraction during SDO events, likely correlated with the marine contribution. However, these samples have lower oxidative potentials, at least in the water soluble fraction, compared with samples rich of OC in the fine fraction.

4. CONCLUSIONS

An analysis of the oxidative potential of the water soluble fraction of $PM_{2.5}$ and PM_{10}, measured using the DTT assay, was performed on the samples collected at the regional GAW station of Lecce (Environmental-Climate Observatory). The OP_{DTT} is used as an indicator of potential health effects associated to oxidative stresses. Measured DTT activities have been correlated with PM concentrations and with the content of OC and EC in collected samples. In addition, FTIR spectroscopy was employed to quantify organic matter (OM) by functional groups and to investigate the presence of carbonates in collected samples.

Results indicate that mass-normalized OP_{DTT} is generally larger on $PM_{2.5}$ than on PM_{10}, however, the differences among the two fractions are minimized for particulate matter with high carbon content. The advection of Saharan dust brings large contributions of coarse particles with relatively high OC concentration. However, the OP_{DTT} during these events is significantly lower (for the PM_{10} fraction) than the average value and the differences between the two size fractions are maximized with larger DTT activities observed in the fine fraction ($PM_{2.5}$).

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