WATER SOLUBLE ORGANIC CARBON (WSOC) CONTENT AND REDOX ACTIVITY OF SIZE-SEGREGATED PM IN THESSALONIKI, NORTHERN GREECE

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ABSTRACT

Size-segregated ambient PM samples were collected from two sites, an urban traffic site and an urban background site, during January-February 2013 (winter sampling period) and May-June 2013 (summer sampling period), in Thessaloniki. PM was separated into four fractions by their aerodynamic diameter >3, 0.95-3, 0.95-0.49 and <0.49 μm. PM samples were analysed for WSOC with a TOC-analyser and redox activity was measured using the dithiothreitol (DTT) assay.

Mean total WSOC concentrations (sum of all size fractions) at the urban traffic site was 2.68 μg m^{-3} in summer *vs.* 5.65 μg m^{-3} in winter. Corresponding values at the urban background site were significantly lower (1.34 μg m^{-3} in summer *vs.* 3.31 μg m^{-3} in winter).The higher WSOC concentrations in winter could be attributed to anthropogenic sources suggesting contribution from residential heating facilities, as well as to lower inversion heights and limited chemical and photochemical degradation. In both sampling campaigns, WSOC concentrations increased steadily with decreasing particle size, especially at the urban traffic site, and maximum concentrations were associated with the smallest particle size fraction <0.49 μm, that is highly related to a potential health risk.

Mean total Redox Activity (sum of all size fractions) at the urban traffic site was 0.67 and 0.54 nmole DTT/min*μg in summer and winter, respectively. Corresponding values at the urban background site were higher than at the traffic site (0.72 and 1.2 nmole DTT/min*μg in summer and winter, respectively). Redox activity was highest in 0.49-0.95 μm fraction at both sites and in both sampling periods. Redox activity was significantly ($p<0.05$) correlated with WSOC only in the fraction of <0.49 μm in winter at the traffic site. Correlations with water soluble trace elements and water soluble ions were also assessed.

Keywords: water soluble organic carbon, DTT assay, PM, redox activity, urban traffic and background site.

1. Introduction

Organic and elemental carbon (OC and EC, respectively) constitute major components of atmospheric particulate matter (PM), with a sum contribution in European urban areas reaching up to 25‑40% and 30‑50 % of total PM10 and PM2.5 masses, respectively. Water-soluble organic carbon (WSOC) represents a significant fraction (30-70%) of OC. WSOC in aerosols usually has several different sources, including primary emissions from biomass burning and fossil fuel combustion, as well as photochemical oxidation of organic precursors of both anthropogenic and biogenic origin (Du *et al*., 2014). The redox activity of PM is usually assessed by its ability to catalyze the reduction of oxygen by dithiothreitol (DTT). The DTT assay is considered to be a reliable measure of the redox activity of particles, by determining the capacity of PM samples to catalyze ROS generation, inducing oxidative stress. The relationship between redox activity and chemical composition of PM needs further clarification (Tsakiri *et al*., 2011).

The present study aimed at the determination of WSOC and the DTT-based redox activity of size-segragated airborne PM at two urban sites within the city of Thessaloniki, in northern Greece, and examine their spatiotemporal variations and correlations with other water soluble components.

2. Materials and methods

Sample acquisition was performed during winter and summer 2013 at an urban traffic site and an urban background site in the agglomeration of Thessaloniki, northern Greece. Four particle size fractions (>3, 0.95-3, 0.95-0.49 and <0.49 μm) were separated using a 3-stage high volume impactor (Sierra instruments, model 235) operated at a constant flow rate of 1.1 m^3 min^{-1}. Quartz filters (Environmental Tisch TE-230QZ) were used as impaction substrates, (slotted 5.7 x 5.7 cm) for the three coarser size fractions and rectangular backup filters (2500QATUP) for the finest size fraction. Preceding sampling, filters were baked at 450 °C for 5 h, wrapped in aluminum foil and sealed in polyethylene zip bags. The sample collection time was 48 hours.

Loaded filters were ultrasonically extracted with ultrapure Milli-Q water and filtrated through 0.45 μm pore membranes. The determination of WSOC was carried out by using in a Shimadzu TOC–VCSH Analyzer by using the NPOC procedure.

A detailed description of the DTT assay is reported by other researchers (Tsakiri *et al*., 2011). Briefly, aqueous PM extracts were incubated with DDT (1 mM) in phosphate buffer (0.5 M, pH 7.4) for various time periods from 0 to 40 minutes. At the specific times, 10% trichloroacetic acid was added so as to stop the reaction. Then, an aliquot of the mixture was mixed with Tris HCl (0.4 M, pH 8.9), containing 20 mM EDTA and 10 mM DTNB (5,5′-dithiobis-2-nitrobenzoic acid) solution. The absorption of the formed 5-mercapto-2-nitrobenzoic acid at 412 nm was measured, in order to determine the concentration of the remaining DTT.

The statistical program SPSS20 was used for the statistical analysis of analytical data.

3. Results

3.1. Water soluble organic carbon

Figure 1 presents the mean concentrations of WSOC during the sampling campaigns at the two sites.

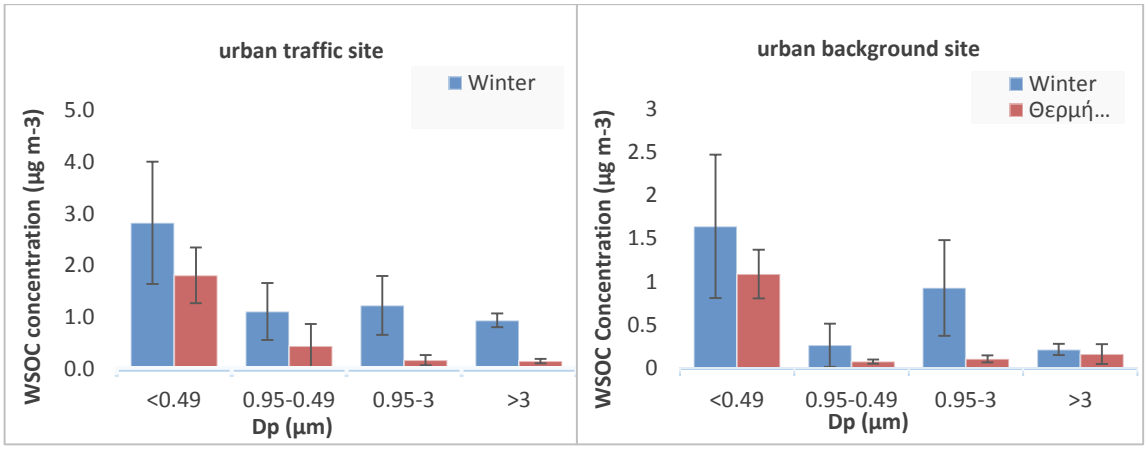

Figure 1: Mean concentrations of WSOC (μg m^{-3}) during the sampling campaigns.

The mean total WSOC (sum of all size fractions) varied between 6.10 μg m^{-3} in winter and 2.63 μg m^{-3} in summer, respectively, for the urban traffic site, while at the urban background site, WSOC was 3.06 μg m^{-3} in the cold period and 1.44 μg m^{-3} in the warm season, respectively. The concentrations of WSOC were higher during winter compared to summer values, suggesting increased emissions of OC from domestic heating (Decesari *et al*., 2002). Higher wintertime levels of WSOC have also been reported in other studies conducted in Thessaloniki (11.4 *vs.* 7.59 μg m^{-3} in TSP, Chrysikou, 2009; 4.77 *vs.* 3.66 μg m^{-3} in PM_{10}, Flarountzou *et al*., 2008), as well as in other cities.

In all samples, the particulate fraction <0.49μm represents the largest percentage of the total concentration of WSOC (40-56% and 63-79% in the cold and the warm period, respectively). The particulate fraction <0.95 μm, representing the alveolar fraction of particles, accounts for 59% (cold period) and 82% (warm period) of WSOC. Similarly, at the urban background site, the

particulate fraction <0.49 μm represents the largest percentage of the total concentration of WSOC (19-63% and 63-83% for cold and warm period, respectively). The particulate fraction <0.95 μm represents 63% (cold season) and 81% (warm period) of total water soluble organic carbon.

Association of WSOC with the quasi-ultrafine particles suggests that gas-to-particle conversion of anthropogenic VOCs may be an important secondary formation pathway. Nevertheless, the second peak in 0.95-1.5 μm that was apparent in winter at the urban background site suggest that wood burning emissions may represent a primary source of WSOC (Decesari *et al*., 2001). Previous size-resolved measurements of WSOC in Thessaloniki showed maximum concentrations in the <0.95 μm size fraction in both the cold and the warm period (Chrysikou, 2009), whereas at the outskirts of Bologna the maximum WSOC concentration was found in 0.42-1.20 μm in the cold period and in <0.42 μm in the warm period (Matta *et al*., 2003).

3.2. Redox activity

The intrinsic DTT redox activity (nmol $min^{-1}\mu g^{-1}$) of the particle size fractions at the two sampling sites is shown in Fig.2. All size fractions exhibited measurable redox activity. The highest values were in most cases observed in particles 0.49-0.95 μm (with the exception of winter samples in urban traffic site, in which maximum redox activity appeared in larger particles, 0.95-3μm), suggesting that these particles are enriched with components capable of producing ROS formation and oxidative stress.

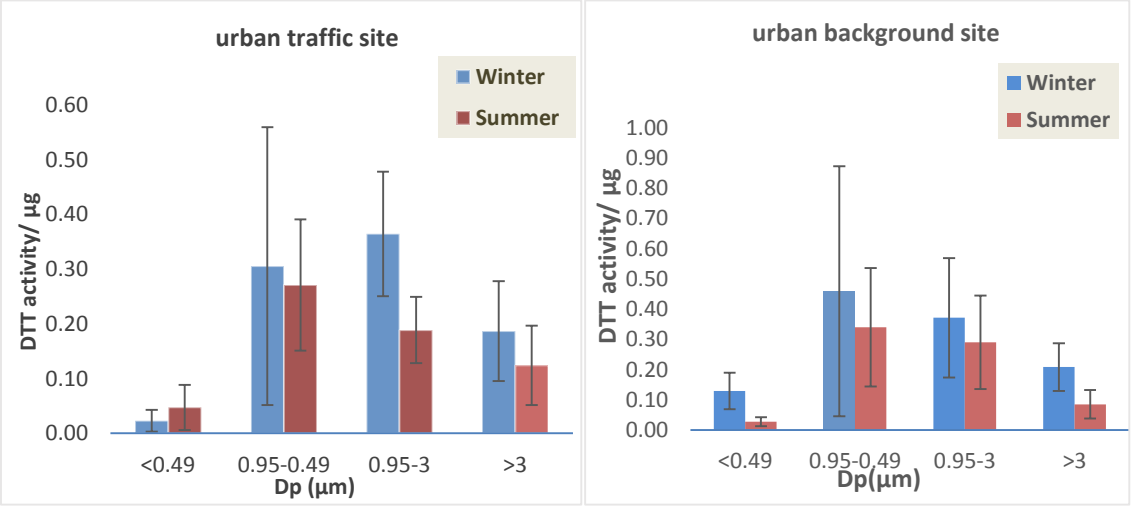

Figure 2: Redox activity of size-fractionated PM samples (nmol $min^{-1}\mu g^{-1}$).

In many studies, the highest DTT activity of PM has been allocated to the ultrafine particle size range (Cho *et al*., 2005; Ntziachristos *et al*., 2007). Redox activity values measured in quasi-UPFs at various sites across the Los Angeles basin were in the range 0.03 - 0.11 nmol $min^{-1}\mu g^{-1}$ with noticeable peaks at sites impacted by fresh traffic emissions (Saffari *et al*., 2014). However, in Rotterdam, Netherlands, this was true only at stop and go traffic sites, whereas at continuous/truck traffic and urban background sites $PM_{2.5}$ exhibited higher redox potential than quasi-UPFs (Steenhof *et al*., 2011). Correspondingly, the redox activity of PM_{10} previously measured at other urban sites in Thessaloniki (Tsakiri *et al*., 2011) was relatively lower than those measured in PM2.5 (0.006 - 0.021 *vs.* 0.018 - 0.038 nmol $min^{-1}\mu g^{-1}$, respectively), whereas the redox activity of the coarse ($PM_{2.5-10}$) fraction was even lower (0.013 - 0.018 nmol $min^{-1}\mu g^{-1}$). Previous size-resolved redox activity measurements in Thessaloniki indicated highest values in the submicron size fraction, <0.95 μm (Chrysikou and Samara, 2009).

For all particle fractions at the urban traffic site, the average redox activity was higher during the cold period except for the <0.49μm fraction that exhibited a higher average value in the warm period. However, the seasonal variation of redox activity of total particles at the urban traffic site showed no statistical significance ($p>0.05$). At the urban background site, the particulate fractions

0.49-0.95 and 0.95-3 μm follow the same trend as the urban traffic site and therefore the average concentration of particles is greater during the cold period. It was also observed that the seasonal variation of redox activity of total particles in the urban background site showed no statistical significance ($p>0.05$).

3.3. Correlations of redox activity with WSOC, water soluble trace metals and ions

A statistical analysis of correlations of redox activity with WSOC and water soluble trace metals (Ba, Cd, Cu, Fe, Pb, Mn, Ni, Zn, Cr, Al, As, Ru, Ir, Ca, Mg, Pt, Pd, Rh) and ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) was performed. During winter at the traffic site, significant statistical correlation ($p<0.05$) was found for redox activity with WSOC in the particles <0.49μm ($r=0.894$). Good correlation of WSOC with redox activity has been observed also by Verma *et al*. (2009), according to which the increase of solubility of organic compounds, induced by photochemical oxidants during the formation of secondary organic aerosol, enhances the ability of suspended particles to generate free radicals. Good correlations, in this study, were also observed in summer at the urban traffic site between redox activity and water soluble elements such as As in 0.49-0.95μm fraction ($r=0.882$), and with Ba, Cd, As, Rh in the 0.95-3μm ($r=0.900$-0.978). At the urban background site, redox activity was not found to correlate significantly with any of water soluble chemical components.

4. Conclusions

The WSOC and the DTT-based redox activity were determined in size-segregated aerosol particles at an urban traffic and αv urban background site during the cold and the warm period. The total concentrations of WSOC were higher in winter than in summer probably due to higher emissions from wintertime sources such as domestic heating. At both sites and in both sampling periods, redox activity was highest in the 0.49-0.95 μm fraction suggesting that particles in this fraction are enriched with components that are capable to produce ROS formation and oxidative stress. Redox activity was significantly ($p<0.05$) correlated with WSOC only in the <0.49 μm fraction of PM at the traffic site in winter. Strong correlations of redox activity and water soluble trace metals were also observed at this site in the warm period.

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