### Chemical and toxicological characterization of the water soluble fraction of size-resolved urban particulate matter

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Chemical and toxicological characterization of the water soluble (WS) fraction of size-resolved particulate matter (PM) (<0.49, 0.49-0.97, 0.97-1.5, 1.5-3.0, 3.0-7.2 and >7.2μm) was carried out at two urban sites in Thessaloniki, northern Greece. Chemical characterization included water soluble organic carbon (WSOC), ions (NO3−, SO42−, Cl−, Na+, NH4+, K+, Mg2+, Ca2+) and trace elements (Al, As, Ba, Cd, Cr, Cu, Fe, Pb, Mn, Ni, Zn, Pt, Pd, Rh, Ru, Ir, Ca, and Mg). The dithiothreitol (DTT) assay was employed for the abiotic redox activity assessment of water soluble PM. Cytotoxic responses in human lung cells (MRC-5) were investigated by employing the mitochondrial dehydrogenase (MTT) bioassay, while DNA damage was estimated by single cell gel electrophoresis (Comet assay). Ccytogenetic effects were examined on human chromosomes and cells (lymphocyte cultures) by measuring the sister chromatid exchanges (SCEs), as well as the Proliferation Rate Index (PRI) and the Mitotic index (MI).

Wintertime PM at the traffic site was characterized by significantly lower WS fraction in comparison to the urban background site (7-31% *vs.* 18-56%) peaking in finer sizes as well (0.49-0.97 μm *vs.* 0.97-1.5 μm). At both sites, WS PM fraction increased during summer (18-79% and 15-90% at the traffic and the background site) with a shift to larger particle sizes (>3 μm and 0.97-3 μm, respectively). Ions were the most abundant WS constituents accounting on average for 6-28% of PM mass at the traffic site with maximum content in 0.49-0.97 μm. The corresponding values at the urban background site were relatively higher (11-41%) maximized in larger particles (0.97-1.5 μm). WSOC accounted on average for 0.9-9.3% and 1.2-20% of PM mass at the traffic and the urban background site, respectively, presenting maximum content in 0.49-0.97 μm with the exception of the background site in winter, where maximized in larger particles (0.97-1.5 μm). Total elemental mass in winter accounted for 0.03-0.23% and 0.07-0.34% of PM mass at the traffic and the urban background site, presenting maximum content in 0.49-0.97 μm and 0.97-1.5 μm, respectively. The corresponding contents in summer were relatively higher (0.15-2.5% and 0.5-2.6 % at the traffic and the background site) with a shift of the maximum content to larger particle sizes (>3 μm and 0.97-3 μm).

DTT-based redox activity was higher at the urban background site (0.122-0.459 and 0.028-0.340 nmol min-1μg-1, in the cold and the warm period, respectively) than at the traffic site (0.023-0.306 and 0.047-0.271 nmol min-1μg-1, in the cold and the warm period, respectively) being highest in 0.49-0.97 μm. WSOC correlated significantly with redox activity only in winter suggesting that the increased water-soluble organic aerosols of both primary (e.g., biomass burning) and secondary origin enhance the oxidative potential of ambient PM. MTT-based cytotoxicity of all particle size fractions in winter were 3-5 times higher at the traffic than the background site. In summer, cytotoxicity was similar at the two sites for most size ranges, with the exception of 1.5-3 μm that showed higher (~2-fold) cytotoxicity at the background site. Chemical that correlated with the cytotoxicity were Fe and Zn at the traffic site in summer, as well as Ba and NH4+ at the background site in winter and summer, respectively. LDH activity in all samples was negligible, suggesting that aqueous PM extracts do not affect the integrity of the plasma membrane.

WS fractions of fine particles (0.97-3 μm) displayed increased SCEs per metaphase, as well as elevated cytostaticity and cytotoxicity effects. Mutagenic to man were found to be particularly wintertime fine particles at the urban background site implying contribution from residential wood burning.

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