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Redox activity and chemical speciation of size fractionated PM in the communities of the Los Angeles-Long Beach harbor

S. Hu¹, A. Polidori¹, M. Arhami¹, M. M. Shafer², J. J. Schauer², A. Cho³, and C. Sioutas¹

¹University of Southern California, Department of Civil and Environmental Engineering, 3620 South Vermont Avenue, Los Angeles, CA 90089, USA

²University of Wisconsin-Madison, Environmental Chemistry and Technology Program, 660 North Park Street, Madison, WI 53706, USA

³University of California, Los Angeles, School of Medicine, Los Angeles, CA 90095, USA

Abstract. In this study, two different types of assays were used to quantitatively measure the redox activity of PM and to examine its intrinsic toxicity: 1) in vitro exposure to rat alveolar macrophage (AM) cells using dichlorofluorescein diacetate (DCFH-DA) as the fluorescent probe (macrophage ROS assay), and: 2) consumption of dithiothreitol (DTT) in a cell-free system (DTT assay). Coarse (PM_{10-2.5}), accumulation (PM_{2.5-0.25}), and quasi-ultrafine (quasi-UF, PM_{0.25}) mode particles were collected weekly at five sampling sites in the Los Angeles-Long Beach harbor and at one site near the University of Southern California campus (urban site). All PM samples were analyzed for organic (total and water-soluble) and elemental carbon, organic species, inorganic ions, and total and water-soluble elements. Quasi-UF mode particles showed the highest redox activity at all Long Beach sites (on both a per-mass and per-air volume basis). A significant association ($R^2=0.61$) was observed between the two assays, indicating that macrophage ROS and DTT levels are affected at least partially by similar PM species. Relatively small variation was observed for the DTT measurements across all size fractions and sites, whereas macrophage ROS levels showed more significant ranges across the three different particle size modes and throughout the sites (coefficients of variation, or CVs, were 0.35, 0.24 and 0.53 for quasi-UF, accumulation, and coarse mode particles, respectively). Association between the PM constituents and the redox activity was further investigated using multiple linear regression models. The results showed that OC was the most important component influencing the DTT activity of PM samples. The variability of macrophage ROS was explained by changes in OC concentrations and water-soluble vanadium (probably originating from ship emissions – bunker oil combustion). The multiple regression models were used to predict the average diurnal DTT levels as a function of the OC concentration at one of the sampling sites.

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