Contributions of Some Cytokine Active Metals in Ambient Particles Attributed to Coal Combustion by CMB

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Summary

Recent epidemiologic studies have shown that short-term increases in urban airborne particle mass concentrations are associated with increased mortality and morbidity from respiratory and cardiovascular diseases, even at respirable particle mass concentrations below the previous PM10 National Ambient Air Quality Standard. Compelling evidence suggests that water- soluble metal components of urban PM are important determinants of the respiratory effects observed during air pollution episodes. Metals, particularly reactive transition metals such as V, Zn, Fe, Cu, and possibly Hg, associated with submicrometer aerosol particles may directly initiate or exacerbate irritation of respiratory tissues by stimulating local cells to release reactive oxygen species (ROS, e.g., hydrogen peroxide and superoxide free radicals) and inflammatory mediators, such as cytokines like TNFα and IL-6. Various studies indicate that the water-soluble inorganic compounds exert the most profound effects. Others attribute the response to specific metals. A study by Adamson et al. suggests that Zn but not Cu, Fe, Al, Pb, Mg, or Ni accounted for the inflammatory response induced by an atmospheric dust sample. Moreover, Carter et al. (10) suggest that the dose of soluble metals, not particulate mass, relates most closely with associated cardio-pulomonary effects in healthy and compromised hosts. These observations are especially important in view of the fact that the masses of various inorganic constituents, including first-series transition metals capable of producing ROS, are predominately associated with **primary** aerosol emissions from high-temperature combustion sources (HTCS), such as coal- and oil-fired power plants (CFPP and OFPP), municipal and medical incinerators, diesel powered vehicles, and residential furnaces, and are, thus, more highly elevated near local sources, than is usually the case for interregionally transported air. Moreover, these primary components comprise only a small fraction of the respirable aerosol mass.

Herein, we report concentrations of metals resolved by size and by source using CMB methods applied to size segregated aerosol samples collected in ambient Baltimore, MD, air using micro-orifice impactors and analyzed by instrumental neutron activation analysis (32 elements) and X-ray Fluorescence (Pb and S). The data are interpreted in the context of discrete aerosol populations observed in plumes of nearby HTCSs. Size-fractionated aerosol samples were collected with micro-orifice impactors (MOI) to provide 10 discrete particle fractions with midpoint diameters estimated as follows: 21.2, 6.9, 2.4, 1.3, 0.74, 0.40, 0.22, 0.12, 0.070, and 0.033 µm. Six 12-hour (6:00 AM to 6:00 PM) MOI samples (60 individual stages) collected in August, 1995, on the roof of the Eastern Avenue Fire Station in Downtown Baltimore, were selected for Chemical Mass Balance (CMB) analysis. More than 40 industrial sources, including a steel mill, are located along the Patapsco river in Baltimore's southeastern quadrant, 3 km south of the site. On the basis of AIRS data, 31% of PM2.5 emissions in Maryland are attributed to the steel mill, while 29% are attributed to Bay-area electric power plants.

Results of the CMB suggest that utility coal combustion is the major source for four of the elements (i.e., Al, Ce, Se, and W); none for which activity in cytokine assays has been reported. Aluminum and other crustal species (Ce and La) are surely emitted as residual silicate mineral matter that escapes the control devices, but even these contributions are each <28% of the total ambient concentrations. Utility coal combustion is clearly the largest single source of atmospheric Se in Baltimore, however, Se is a micronutrient and antioxidant, and hence not expected to be detrimental to health. In College Park, maximum Se concentrations observed during influence of the plume from the

coal-fired power station in Alexandria, VA, 20 km downwind, were about 6 ng/m^3,[29] i.e., a concentration which would deliver a Se dose equivalent to that found in common daily vitamin supplements. Furthermore, it is well known that a substantial fraction of the Se in coal is emitted to the atmosphere in the vapor phase, which upon emission becomes associated with primary particles in the near plume (30). The 30% underprediction of the observed average Se concentration could, thus, well reflect the gas phase component. If so, then the concentrations predicted for the coal source should be reduced by 30% to reflect the true source profile. Coal contributions for As, Co, Cr, Fe, and Ti range from 11 to 20% of their total atmospheric burdens and, likewise, may be 30% less than these values. The coal combustion fraction attributed to Cs (11%) could be even less still, as Cs is over-predicted by a factor of 1.9.

Although coal-combustion is predicted to be the largest source of fine particle W (63%) in Baltimore, the average W concentration was over predicted by nearly 10-fold and, thus, the CMB result for this element must be viewed as highly suspect. Furthermore, size spectra for W and Se for the MOI sample of August 14th, show that W concentrations were sometimes influenced by a nearby source emitting W-laden particles with a modal diameter of approximately 0.1 μm. While peaks in W spectra often correlated with those of Se, there were clearly other sources. On August 14th, W mass in 0.1-μm particles, in fact, substantially exceeded its mass in the region of the Se peak. The lack of an analogous peak for Se at this diameter indicates that this source is not a coal-fired power plant. The lack of a corresponding peak in either the V, Zn or Se spectra (i.e., markers of oil combustion, incinerators, and coal combustion), suggests that, in addition to its total fine-particle concentration being over predicted, the fraction of W attributed to coal combustion is also over predicted.

Chemical Mass Balance calculations for size-segregated Baltimore Aerosol suggest that contributions of coal-combustion sources to ambient transition metal burdens are small relative to other sources. This is especially true for metals shown to elicit cytokine responses, i.e., V and Zn, in either cell- or animal tests. Resolution of the fine particle composition by size is shown to improve interpretation of CMB results.