

**Determination of Particle-Bound PAHs in Outdoor Air using Accelerated Solvent Extraction and Isotope Dilution GC/MS**Zheng Li<sup>1</sup>, James Mulholland<sup>2</sup>, Courtney D Sandau<sup>3</sup>, Ted Russell<sup>2</sup>, Donald G Patterson Jr.<sup>1</sup>, Andreas Sjödin<sup>1</sup><sup>1</sup>Centers for Disease Control and Prevention<sup>2</sup>Georgia Institute of Technology<sup>3</sup>Jacques Whitford Limited

Fine particulate air pollution has been linked to health effects, such as respiratory and cardiopulmonary problems. PM 2.5, fine particles with diameter 2.5  $\mu\text{m}$  or smaller, are especially of concern because when inhaled, they can penetrate deeply into the lungs. Further, the association of fine particles with mutagenic and carcinogenic chemicals, such as polycyclic aromatic hydrocarbons (PAHs), may increase the potential for adverse health effects.

We are reporting on the development of a robust and accurate method for measuring particle-bound PAHs using accelerated solvent extraction (ASE) and isotope dilution GC/MS. In this method, we have included the 16 EPA primary PAHs, as well as benzo[c]phenanthrene, benzo[e]pyrene, perylene, and retene, a proposed wood smoke marker. Quantification is made using 16 <sup>13</sup>C-labeled PAHs as internal standards, spiked to all air filter samples before extraction, to account for losses during sample preparation and instrument variability. Filter samples were extracted by dichloromethane (DCM) using ASE (Dionex Corp., Sunnyvale, CA) which is a pressurized liquid extraction system. The DCM extracts were concentrated to ~ 50  $\mu\text{L}$  under a gentle stream of nitrogen and spiked with <sup>13</sup>C-labeled 3'-MeO-2,2',3,4,4',4'-hexachlorobiphenyl as the recovery reference standard. Final analysis was performed on a gas chromatography/mass selective detector system (GC/MSD, Agilent Technologies, Atlanta, GA) using the selective ion monitoring mode. Different GC columns were tested, and the method was optimized to achieve full separation of all the 20 PAH analytes and 16 <sup>13</sup>C-labeled internal standards using a RTX-440 column (Restek Corp., Bellefonte, PA). Calibration curves for all analytes demonstrated linearity of the GC/MS quantification system over 3 orders of magnitude (5-5000  $\text{pg}/\mu\text{L}$ ). The ASE method was compared to sonication-assisted extraction, a more traditional technique, and was found to give similar results. ASE is preferred since it is automated and more time-efficient; also, it does not require a filtration step that is necessary after the sonication extraction.

24-Hour air filter samples (16.7 L/min), taken daily from two urban sites and a rural site around the metro Atlanta area in June and December of 2003, were measured for the 20 PAHs. Total toxicity equivalences (TEQ's) associated with the particle-bound PAH fractions were calculated. Distinct spatial and seasonal variations were observed; e.g. urban sites had higher particulate phase PAH levels than rural sites, and levels were higher in winter than in summer. Median concentrations for total particulate PAHs were 2.1, 1.5, 0.2  $\text{ng}/\text{m}^3$  for the two urban sites and the rural sites, respectively. The differences were statistically significant (Mann-Whitney U-test) between the urban and rural sites ( $p < 0.01$ ), but not significant between the two urban sites ( $p = 0.6$ ). Particulate PAH level in winter (4.2  $\text{ng}/\text{m}^3$ ) was significantly higher than in summer (1.2  $\text{ng}/\text{m}^3$ ,  $p < 0.001$ ). Total PAH concentrations were found to be correlated (Spearman Rank Order Correlations) with organic carbon ( $S_R = 0.35$ ,  $p < 0.001$ ) and elemental carbon ( $S_R = 0.27$ ,  $p < 0.01$ ), but not correlated with PM2.5 ( $p > 0.05$ ). The correlations using only winter data were even stronger; correlation coefficients were 0.87 and 0.84 between PAH and OC, EC respectively ( $p < 0.001$ ). Levels of retene were correlated with potassium ( $S_R = 0.57$ ,  $p < 0.001$ , winter data), the marker used for biomass burning source apportionment in most chemical mass balance models, suggesting that retene can potentially be used as a marker for biomass burning.