

**COLLABORATIVE RESEARCH: Study of Aerosol Sources and Processing
at the GVAX Pantnagar Supersite**

Final Report

Covering the Period 4/15/2011 to 4/14/2014

Principal Investigator: Professor Joel A. Thornton thornton@atmos.uw.edu
Department of Atmospheric Sciences
University of Washington
Seattle WA, 98195

DOE/Office of Science Program Office: Office of Biological and Environmental Research

DOE/Office of Science Program Technical Contact: Dr. Ashley Williamson

DOE Award No. DE-SC0006036

1. Executive Summary (some parts repeated from PI Worsnop's final report)

This project funded the participation of scientists from seven research groups, running more than thirty instruments, in the Winter Intensive Operating Period (January-February 2012) of the Clean Air for London (ClearfLo) campaign at a rural site in Detling, UK, 45 km southeast of central London. The primary science questions for the ClearfLo Winter IOP were, 1) what is the urban increment of particulate matter (PM) and other pollutants in the greater London area, and, 2) what is the contribution of solid fuel use for home heating to wintertime PM? An additional motivation for the Detling measurements was the question of whether coatings on black carbon particles enhance absorption.

The UW contribution by PI Thornton's group was to make the first deployment of a chemical ionization mass spectrometer instrument (MOVI-CI-ToFMS) to measure both particle and gas phase organic acids. The new instrument ran nearly continuously during the ClearfLo WINTER IOP at the Detling site, producing a first-ever data set of molecular composition information that can be used for source apportionment and process studies.

Analysis of the MOVI-CI-ToFMS dataset acquired in Detling is ongoing by collaborators from the U. Manchester in London. The UW group published a paper in *Environmental Science and Technology* and contributed to another (Bohnenstengel et al BAMS 2015) detailing a direct molecular connection between biomass/biofuel burning particles and aerosol absorption. The ES&T paper (Mohr, et al ES&T 2013) has received 42 citations in just 3 years indicative of its significant impact on the field. These measurements of urban and rural aerosol properties will contribute to improved modeling of regional aerosol emissions, and of atmospheric aging and removal.

4. Project Schedule

Year	Proposed Task	Progress
Year 1	Prepare, calibrate and integrate MOVI-CI-ToF-MS instrument for deployment.	Containers deployed to Detling, UK for Jan-Feb, 2012 measurement campaign.
Year 2	Deploy containers to Pantnagar, India and make measurements. Preliminary data analysis and quality assurance.	UK deployment concluded, preliminary data analysis and quality assurance completed, final data analysis started.
Year 3	Analysis of field data and publication of results.	Final data analysis by UW completed, ongoing analysis by collaborators. Data posted to BADC archive and ARM archive. Two articles published, others in preparation.

2. Project Activities (some repeated from PI Worsnop's collaborative report)

This project was originally funded as a supersite in Pantnagar, India to complement the cloud and aerosol properties measured by the AMF 1 at the Nainital Observatory in India during the Ganges Valley Aerosol Experiment (GVAX). The Pantnagar site project was cancelled in late November, 2011, shortly before the scheduled shipment of instruments to India. We were approved to participate instead in the Clear Air for London (ClearfLo) campaign in January and

February, 2012. ClearfLo is a large, multidisciplinary study of the London urban atmosphere aimed at understanding the relationships between surface meteorology, gas-phase composition and particulate matter at a city street site, a city background site (away from local traffic sources) and at a rural location that samples the outflow from the London megacity. In addition to year long measurements, two intensive operating periods (IOPs) were planned for January-February and July-August, 2012. The winter time studies also provide information on gas and particle emissions from home heating solid fuels. The ClearfLo project is coordinated by the UK National Centre for Atmospheric Science with support from the UK Natural Environment Research Council.

The collaborators deployed a suite of instruments to measure particulate chemical composition, including organics, inorganics and black carbon, size distributions, optical properties and hygroscopic properties, as well as gas-phase oxidants and aerosol precursors, at the rural site southeast of London at Detling, UK during the January-February, 2012 intensive (Figure 1). A specific focus of this collaborative campaign was to improve our understanding of sources of aerosol light absorption.

The University of Washington, Seattle (UW) deployed a newly developed, high sensitivity mass spectrometer system (MOVI-CI-TOFMS) that is capable of near real-time measurements of molecular level composition of both gas and particle-phase organics. Several research groups joined together to provide the Detling rural site with continuous, high time resolution measurements of aerosol chemistry and microphysics, measurements of gas-phase tracers and secondary organic aerosol (SOA) precursors, and radiative and meteorological measurements. A complete list of instruments that successfully collected data at the Detling site is shown in Table 1 (Courtesy of PI Worsnop's report).

Table 1. Instrument List for ClearfLo Detling, UK site.

Institute / Investigator	Instrument	Species/Parameters Measured
ARI / S. Herndon	2B Tech	O ₃
ARI / S. Herndon	Thermo 42i	NO
ARI / S. Herndon	ARI CAPS	NO ₂
ARI / S. Herndon	Licor	CO ₂
ARI / S. Herndon	ARI QCL	CO, N ₂ O
ARI / S. Herndon	ARI QCL	NO ₂
CEH / D. Famulari	ARI mini-QCL	N ₂ O, CO ₂ , H ₂ O
LANL / M. Dubey	Picarro CRDS	CH ₄ , CO ₂ , H ₂ O
ARI / S. Herndon	GC-FID	Gas-phase VOC
MSU / W. B. Knighton	PTR-MS	Gas-phase VOC
UW / C. Mohr	ARI MOVI-HR-ToF-CIMS	Gas and particle phase organic acids
GIT / N. L. Ng	ARI HR-ToF-AMS	Nonrefractory, submicron particulate (SO ₄ ⁼ /NO ₃ ⁻ /Cl ⁻ /NH ₄ ⁺ /Organics)
ARI / L. Williams	ARI SP-AMS	Nonrefractory submicron particulate + black carbon
PSI / S. Visser	3-stage Rotating Drum Impactor	Trace elements in PM _{1.0} , PM _{2.5} and PM ₁₀
PSI / P. Zotter	Hi Vol Sampler	¹⁴ C in TC, EC/OC concentrations
LANL / A. Aiken	DMT SP-2	Black carbon number, mass loading and coating thicknesses

PSI / P. Zotter	Magee AE31 Aethalometer	7 wavelength aerosol optical absorption and equivalent black carbon
ARI / L. Williams	Thermo MAAP	Aerosol optical absorption and equivalent black carbon
LANL / A. Aiken	DMT PASS-3	3 wavelength aerosol optical absorption, scattering
ARI / P. Massoli	ARI CAPS PMex 630	Aerosol extinction at 630 nm
LANL / A. Aiken	ARI CAPS PMex 450	Aerosol extinction at 450 nm
LANL / A. Aiken	TSI Laser Particle Sizer 3340	Particle size and number (0.07-10 micrometer)
LANL / A. Aiken	TSI SMPS	Particle size and number (8-600 nm)
ARI / L. Williams	Portamet	T, RH, wind speed and direction
ANL / R. Coulter	Vaisala WXT520 Weather Station	T, RH, wind speed and direction, precip.
ANL / R. Coulter	Micro Pulse Lidar	Cloud base, aerosol extinction via backscatter
ANL / R. Coulter	Pyranometer SPN-1	Total, diffuse radiation
ANL / R. Coulter	SODAR	Wind field up to 400 m
ANL / R. Coulter	MFRSR	Radiance, 7 wavelengths

During Year 1, UW worked to refine the proto-type micro-orifice volatilization impactor (MOVI), which was a means to collect submicron particles and thermally desorb components into a chemical ionization mass spectrometer. We then integrated the instrument into the shipping containers in late fall 2011 and arrived in Detling the first week of January, 2012 for operation.

Figure 2 illustrates an example of the type of data UW collected with the MOVI-CI-ToF-MS. The lower panel shows the time series of a suite of particle phase nitrate phenols, known



Figure 1. Containers (on right), rented portacabins (on left) and sampling tower at Detling, UK site.

tracers of biomass/biofuel burning together with meteorological parameters, trace gases CO and NO_x, particle absorption at 370 nm, and total organic aerosol mass (measured with an AMS) in the upper panels. Clear from this figure is the strong correlation between these biomass burning tracers, total organic aerosol mass and light absorption in the region of “brown carbon” absorption enhancements. These correlations suggest a significant contribution of biomass/biofuel combustion, such as residential wood smoke or agricultural field burning to the total organic aerosol mass loading, which dominated submicron mass. Moreover, they suggest that these tracers, all of which are known to absorb strongly in the UV maybe contributing to the enhanced light absorption at 370 nm.

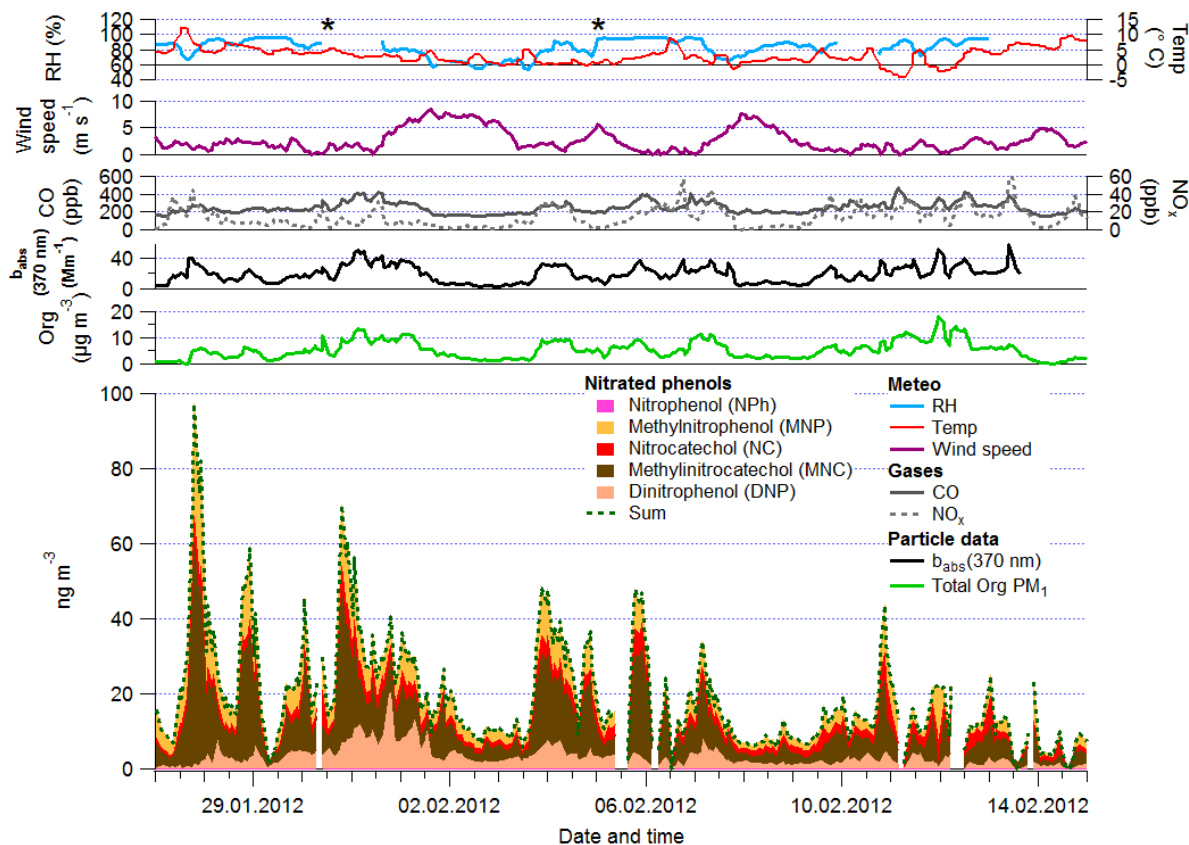


Figure 2: Time series of ambient temperature (Temp) and relative humidity (RH), NO_x, CO, the fraction of babs measured with an aethalometer at 370 nm (babs(370 nm)), total organic PM₁, and particulate nitrated phenols (stacked) as identified by the CIMS during the ClearLo campaign in Detling. The asterisks denote snow fall incidents.

Figure 3 illustrates these correlations both in mass concentration and time of day spaces. The nitrated phenols correlate strongly ($r = 0.6$, panel a) with the AMS derived biomass burning organic aerosol (BBOA) mass spectral factor, independently confirming the attribution of these tracers. Moreover, the diurnal cycle of these tracers and factor are consistent with evening enhancements due to residential heating (panel b). The correlation of the nitrated phenols with the light absorption coefficient at 370 nm ($r = 0.65$ panel c) measured by an aethelometer is of particular interest as this region of the solar spectrum is associated with “brown carbon”, the sources of which have remained uncertain. These results strongly imply that biomass burning is a major source of light absorption at these wavelengths.

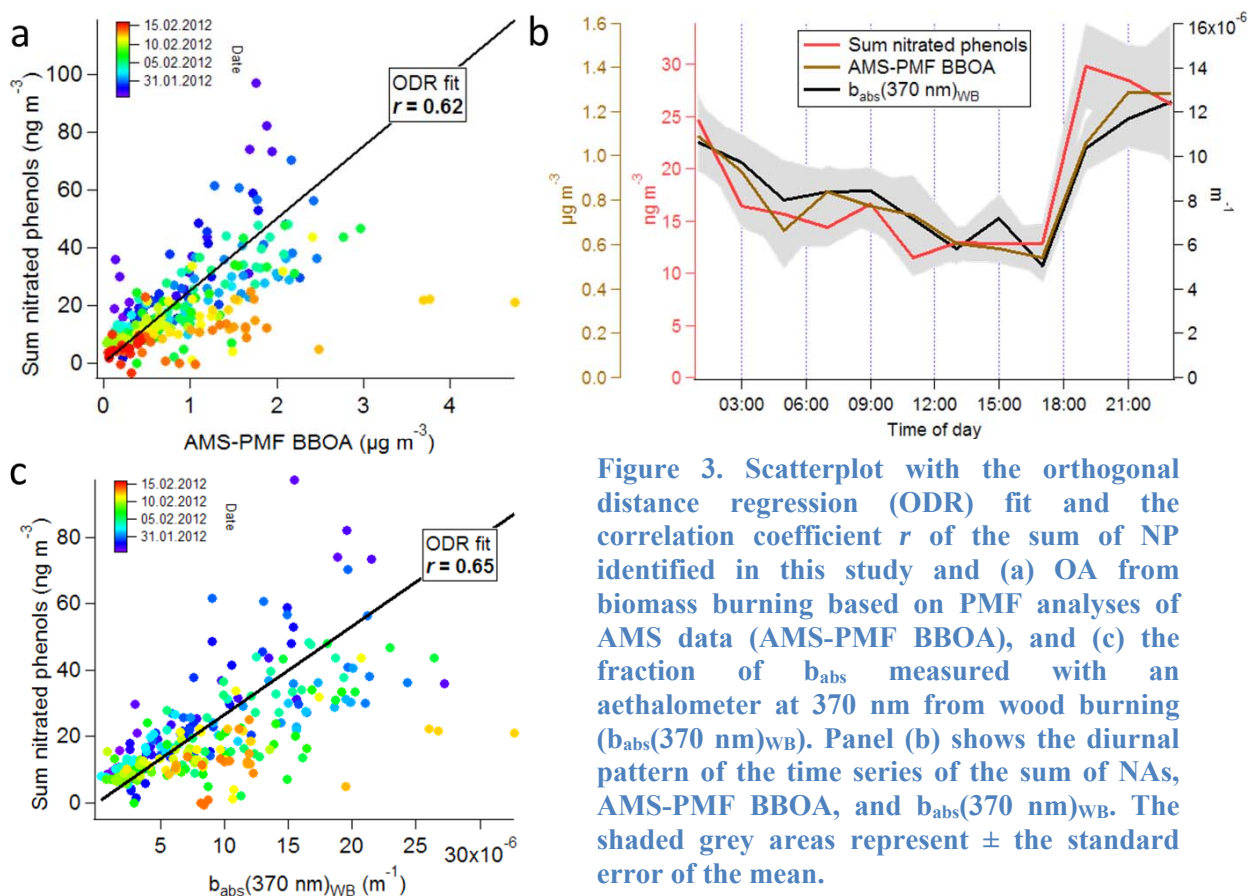
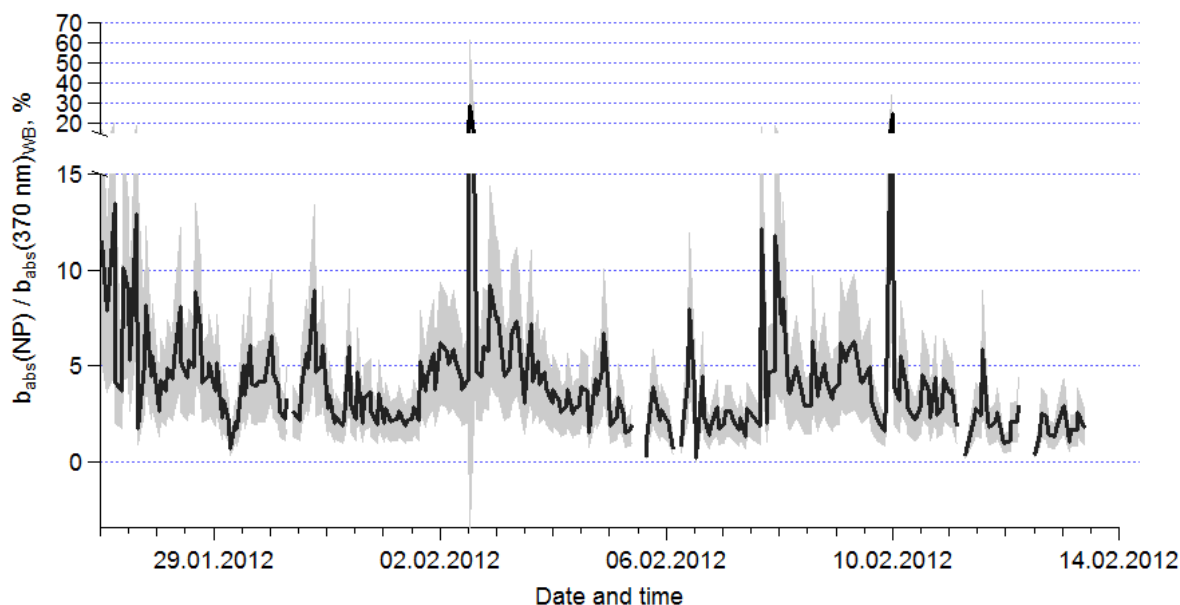


Figure 3. Scatterplot with the orthogonal distance regression (ODR) fit and the correlation coefficient r of the sum of NP identified in this study and (a) OA from biomass burning based on PMF analyses of AMS data (AMS-PMF BBOA), and (c) the fraction of b_{abs} measured with an aethalometer at 370 nm from wood burning ($b_{\text{abs}}(370 \text{ nm})_{\text{WB}}$). Panel (b) shows the diurnal pattern of the time series of the sum of NAs, AMS-PMF BBOA, and $b_{\text{abs}}(370 \text{ nm})_{\text{WB}}$. The shaded grey areas represent $\pm$ the standard error of the mean.

Using the information in Figures 2 and 3, we were then able to put an absolute constraint on the contribution to light absorption caused by the measured nitrated phenols alone. Shown in Figure 4, these calculations suggest we can explain at a molecular level of order 5 – 10% of the light absorption at 370 nm. These findings are important in that our instrument measured other nitrogen containing compounds that correlated with the subset presented in Figure 2, but for which we did not have calibration standards. Thus, we likely could explain an even larger fraction of the light absorption than represented by Figure 4. To our knowledge, such a fundamental description of the light absorption in the UV-VIS range has not been achieved with ambient aerosol particles.



Time series of the percent ratio of the absorption from nitrated phenols ($b_{\text{abs}}(\text{NP})$), based on literature value molecular absorption cross sections, to the total absorption measured by an aethalometer from wood burning carbonaceous matter at 370 nm ($b_{\text{abs}}(370 \text{ nm})_{\text{WB}}$). The shaded areas denote the uncertainty in the ratio based on the $b_{\text{abs}}(370 \text{ nm})_{\text{WB}}$ and $b_{\text{abs}}(\text{NP})$ signals: In addition to the 50% uncertainty of the MOVI-HRToF-CIMS data, measurement values of both time series were assigned a relative error between 0

3. Products

A1. Publications:

Claudia Mohr, Felipe D. Lopez-Hilfiker, Peter Zotter, André S. H. Prévôt, Lu Xu, Nga. L. Ng, Scott C. Herndon, Leah R. Williams, Jonathan P. Franklin, Mark S. Zahniser, Douglas R. Worsnop, W. Berk Knighton, Allison C. Aiken, Kyle J. Gorkowski, Manvendra K. Dubey, James D. Allan, and Joel A. Thornton, Contribution of nitrated phenols to wood burning brown carbon light absorption in Detling, UK during winter time, *Environ. Sci. Technol.*, 2013, 47 (12), pp 6316–6324, DOI: 10.1021/es400683v

Bohnenstengel, S. I.; Belcher, S. E.; Aiken, A.; Allan, J. D.; Allen, G.; Bacak, A.; Bannan, T. J.; Barlow, J. F.; Beddows, D. C. S.; Bloss, W. J.; Booth, A. M.; Chemel, C.; Coceal, O.; Di Marco, C. F.; Dubey, M. K.; Faloon, K. H.; Fleming, Z. L.; Furger, M.; Gietl, J. K.; Graves, R. R.; Green, D. C.; Grimmond, C. S. B.; Halios, C. H.; Hamilton, J. F.; Harrison, R. M.; Heal, M. R.; Heard, D. E.; Helfter, C.; Herndon, S. C.; Holmes, R. E.; Hopkins, J. R.; Jones, A. M.; Kelly, F. J.; Kotthaus, S.; Langford, B.; Lee, J. D.; Leigh, R. J.; Lewis, A. C.; Lidster, R. T.; Lopez-Hilfiker, F. D.; McQuaid, J. B.; Mohr, C.; Monks, P. S.; Nemitz, E.; Ng, N. L.; Percival, C. J.; Prevot, A. S. H.; Ricketts, H. M. A.; Sokhi, R.; Stone, D.; Thornton, J. A.; Tremper, A. H.; Valach, A. C.; Visser, S.; Whalley, L. K.; Williams, L. R.; Xu, L.; Young, D. E.; Zotter, P., METEOROLOGY, AIR QUALITY, AND HEALTH IN LONDON The ClearLo Project. Bulletin of the American Meteorological Society 2015, 96, (5), 779-804.

A2. Presentations:

ASR Science Meeting, Arlington, VA, March, 2012

Oral presentations in breakout session, 5 posters.

American Association for Aerosol Research Annual Meeting, Minneapolis, MN, October, 2012

Poster 2UA.21 Overview of ClearfLo Detling Site: Study of Aerosol Sources and Processing at a Rural Site Southeast of London. LEAH WILLIAMS, Scott Herndon, John Jayne, Andrew Freedman, William Brooks, Jonathan Franklin, Paola Massoli, Edward Fortner, Puneet Chhabra, Mark Zahniser, Harald Stark, Timothy Onasch, Douglas Worsnop, Felipe Lopez-Hilfiker, Claudia Mohr, Joel A. Thornton, Nga Lee Ng, Lu Xu, Matthew Kollman, Berk Knighton, Mavendra Dubey, Allison Aiken, Kyle Gorkowski, Timothy Martin, and Richard Coulter.

ClearfLo Science Meeting, Birmingham, UK, October, 2012

ClearfLo Detling Site: Winter IOP, L. R. Williams, S. Herndon, J. Jayne, A. Freedman, B. Brooks, J. Franklin, P. Massoli, E. Fortner, P. Chhabra, M. Zahniser, H. Stark, T. Onasch, D. R. Worsnop, F. Lopez-Hilfiker, C. Mohr, J. Thornton, N. L. Ng, L. Xu, M. Kollman, B. Knighton, M. Dubey, A. Aiken, K. Gorkowski, T. Martin, R. Coulter, S. Visser, M. Furger, P. Zotter, and A. Prévôt.

ClearfLo Science Meeting, York, UK, March, 2013

ClearfLo Detling Site: Winter IOP, L. R. Williams, S. Herndon, J. Jayne, A. Freedman, B. Brooks, J. Franklin, P. Massoli, E. Fortner, P. Chhabra, M. Zahniser, H. Stark, T. Onasch, D. R. Worsnop, F. Lopez-Hilfiker, C. Mohr, J. Thornton, N. L. Ng, L. Xu, M. Kollman, B. Knighton, M. Dubey, A. Aiken, K. Gorkowski, T. Martin, R. Coulter, S. Visser, M. Furger, P. Zotter, and A. Prévôt.

ASR Science Meeting, Potomac, MD, March, 2013

Oral presentation in breakout session and poster presentation.

American Association for Aerosol Research Annual Meeting, Portland, OR, October, 2013

Oral Presentation 4CA.3. Enhanced Light Absorption by Internally Mixed Atmospheric Black Carbon in Europe. SHANG LIU, Allison Aiken, Kyle Gorkowski, Manvendra Dubey, Scott Herndon, Leah Williams, Paola Massoli, Edward Fortner, Andrew Freedman, Douglas Worsnop, Nga Lee Ng, Claudia Mohr, Felipe Lopez-Hilfiker, Joel Thornton, James Allan, and Christopher Cappa.

Oral Presentation 5CA.6. Black Carbon Containing Particles at a Rural Site Southeast of London, UK during ClearfLo (Winter 2012). LEAH WILLIAMS, Scott Herndon, John Jayne, Andrew Freedman, William Brooks, Jonathan Franklin, Paola Massoli, Edward Fortner, Puneet Chhabra, Mark Zahniser, Timothy Onasch, Manjula Canagaratna, Douglas Worsnop, Felipe Lopez-Hilfiker, Claudia Mohr, Joel Thornton, Nga Lee Ng, Lu Xu, Berk Knighton, Manvendra Dubey, Allison Aiken, Kyle Gorkowski, Shang Liu, Andre Prévôt, et al.,

European Aerosol Conference, Prague, Czech Republic, September, 2013

Oral Presentation. Black Carbon Containing Particles at a Rural Site Southeast of London during ClearfLo Winter IOP, L. R. Williams, S. Herndon, J. Jayne, A. Freedman, B. Brooks, J. Franklin, P. Massoli, E. Fortner, P. Chhabra, M. Zahniser, H. Stark, T. Onasch, M. R. Canagaratna, D. R. Worsnop, F. Lopez-Hilfiker, C. Mohr, J. Thornton, N. L. Ng, L. Xu, W. B. Knighton, M. Dubey, A. Aiken, K. Gorkowski, S. Liu, T. Martin, R. Coulter, S. Visser, M. Furger, P. Zotter, and A. S. H. Prévôt

B. Websites:

The instrument and personnel lists for the AeroFlo project can be found at:
tinyurl.com/AeroFlo-Detling

Preliminary data was posted at: <https://www.dropbox.com/sh/cqxmujz9wvo5lka/BVg-FTm6XL>

An overview of the ClearfLo project and blog entries for the Detling site can be found at:
<http://www.clearflo.ac.uk/news/>

F. Data:

Final data for trace gas measurements have been posted at the British Atmospheric Data Center (BADC) Archive (badc.nerc.ac.uk/browse/badc/clearflo/data) and at the ARM Data Archive (<http://www.archive.arm.gov/armlogin/login.jsp>). The particle measurement and meteorology data is undergoing final review and will be posted by September, 2014.