



APPENDIX AVAILABLE ON THE HEI WEB SITE

Research Report 165

Allergic Inflammation in the Human Lower Respiratory Tract Affected by Exposure to Diesel Exhaust

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Appendix B. Exposure Atmosphere Monitoring

Note: Appendices Available on the Web may appear in a different order than in the original Investigators' Report, and some remnants of their original names may be apparent. HEI has not changed the content of these documents, only the letter identifier.

Appendix B was originally Appendix A

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APPENDIX B

Exposure Atmosphere Monitoring: Details of Methodology and Results

Particle mass. In each exposure study, samples of particulate matter were collected by low-volume filtration, with sampling ports located as near as practical to subjects' breathing zones, to determine total mass concentration. Pilot tests with sampling at multiple locations within the exposure chamber ruled out substantial internal concentration gradients. Filter samples were weighed pre- and post-exposure in a controlled-environment weighing room, after 24-hr periods of temperature and humidity equilibration.

Elemental Carbon (EC) and Organic Carbon (OC). DEP particle mass is dominated by carbonaceous emissions, so that EC is often utilized as a marker for DE. EC and OC also provide the first level of knowledge in breaking down the chemical composition of DE. EC, a graphitic like substance, is used as a tracer for diesel emissions, and is an indicator of the extent of pyrolysis that has occurred within the engine. OC is a surrogate for the complex organic mixture of chemicals present in DEP, many of which are known to elicit negative responses. ECOC samples were collected for each DE exposure on precleaned (600 C, 5 hrs) 47 mm Tissuquartz filters and analyzed following the National Institute of Occupational Safety and Health (NIOSH) 5040 thermal optical carbon analysis procedures. Sucrose standards and certified methane tanks were used to calibrate the response of the ECOC analyzer.

Two offsetting corrections were applied to the OC data reported here—the positive semi-volatile sorption artifact correction factor and the organic-mass-to-organic-carbon correction factor. The semi-volatile sorption artifact refers to semi-volatile *gaseous* species that are sorbed to the quartz filter media substrate and are typically in the range of 30% to 40% of the organic material on the filter. The organic mass to organic carbon correction allows for extrapolation of organic carbon, a measure of only the carbon content on the filter, to organic mass (OM), which includes all atoms (e.g., H, N, and O) bonded to the carbon atoms. In experience at CE-CERT, for ultra-low-sulfur diesel (ULSD) emissions, the OM/OC ratio ranges from 1.3 to 1.4. These two corrections tend to directly offset one another (for ULSD diesel engines) allowing us to report the “C” content from the quartz filter as “OC”. The correction was validated by comparing the EC and OC on the quartz filter and to the total PM collected on the Teflon filter. A linear regression from over 700 ULSD diesel emissions tests conducted at CE-CERT also indicate that the “offsetting correction” (taking mass C as mass OC) is a good estimate.

Carbonyls. Thirteen carbonyl species were evaluated during each DEP human exposure. They represent the species most commonly associated with vehicular exhaust, including several on the EPA hazardous pollutant (HAPs) list. Carbonyl species were collected on Waters 2,4-dinitrophenylhydrazine (DNPH) cartridges. Analysis was conducted following the Society of Automotive Engineers (SAE) 930412HP (Siegl et al., 1993) method by eluting with 5 mL

acetonitrile and then analyzing the eluent using high performance liquid chromatography with UV-vis absorption spectroscopy. Standards - 30 µg/mL and 3 µg/mL - of all 13 carbonyl species were used to calibrate the system following the quality assurance procedures described in SAE-930412HP.

Light Hydrocarbons. While it was expected that total hydrocarbon emissions from the diesel engine would be small, it was still necessary to identify potential light hydrocarbon gas-phase toxic species. Therefore, light hydrocarbons were collected in Tedlar bags and later on TDS desorption tubes followed by analyses using gas chromatography with flame ionization detection (GC-FID). The analyses method followed the protocols outlined in SAE 930412HP (Siegl et al., 1993).

Semivolatiles and Polyaromatic Hydrocarbons (PAHs). Polyaromatic hydrocarbons are important due to potential mutagenic and carcinogenic effects, and as tracers in chemical mass balance models. Therefore, PAHs samples were routinely collected on both precleaned (5 hours, 600 C) quartz followed by PUF-XAD-PUF tubes. These samples were extracted separately and analyzed using gas chromatography with quadrupole mass spectrometer (GC-MS) detection. Deuterated PAH and alkane spikes were used along with calibration standards to quantify PAH and long alkane emissions during the program. The test program followed the EPA-TO13A test protocol modified for increased sensitivity with a large volume injector.

Particle Size Distribution, Number Concentration. Particle size distributions were collected for each experiment to ensure uniform physical characteristics of the DEP. These measurements were conducted using a Scanning Mobility Particle Sizer (SMPS) that provided electrical mobility measurements from 28 to 730 nm, a range that covers the large accumulation peak of DEP. The instrument also supplied number concentration measurements for the range analyzed. This instrument provided feedback every 80 seconds and was ultimately used to set the dilution ratio and identify when the exposure chamber was stable. The instrument was calibrated with National Institute of Standards and Technology (NIST) traceable polystyrene latex balls with no deviation from the calibration noted over the course of the study. An additional custom built fast scan SMPS (5 – 130 nm) was utilized to confirm the absence of nucleation mode particles. Good agreement between the SMPS systems was observed in the overlapping size ranges. Several micro-orifice uniform-deposit impactor (MOUDI) samples verified that filter based mass measurements were also consistent between the chassis test lab and the exposure system as well as verifying that the human personal emissions were at sizes much greater than the DEP in the system.

Air Monitoring Quality Assurance. Each chemical analysis performed as part of this program followed conventional or slightly modified conventional test protocols for vehicle exhaust. Standards were used wherever practical to quantify concentrations of chemicals (EC,

OC, carbonyls, PAHs, as well as a 23 component mixture for light hydrocarbons) and NIST traceable polystyrene latex particles was used to calibrate the SMPS systems. All flows were calibrated against bubble flowmeters traceable to NIST. The analytical facility was audited by an external auditor as part of this program to verify that common quality assurance and analytical practices were followed. Analytical instruments were calibrated for each batch of samples tested as part of this program with linearity, span, and zero checks performed in conjunction with other ongoing programs.

Results: Volume Size Distribution

The objective of this part of the study was to deliver, as consistently as possible, a representative dilute diesel exhaust having a mass concentration of 100 $\mu\text{g m}^{-3}$. Stable mass concentrations were indeed attained throughout the project, as described in the main report. Therefore, comparison of the volume size distribution of the aerosol across different exposures becomes the most important indicator of success in meeting the objective. Figure A.1 (Figure 2 in main report) is a plot of the average volume size distribution for ***all*** diesel exposures over the course of the program, with the error bars representing a single standard deviation. It shows reasonably good consistency overall. Figure A.2 compares the average volume size distributions for Phase 1 and Phase 2, showing excellent agreement, i.e. no appreciable shift in particle volume characteristics from earlier to later exposure studies. Similarly, Figure A.3 compares average distributions across four seasons, showing no appreciable seasonal variation. Figure A.4 shows the volume size distribution for each individual exposure study. The most noticeable changes in the volume distributions from one study to another occur on the left sides of the curves. These represent the volume contribution of particles considerably smaller than the mean aerosol diameter in this study. These very small particles account for most of the variations in particle number size distributions discussed below.

Results: Number Size Distribution

Figure A.5 is a plot of the average number size distribution for ***all*** diesel exposures, with the error bars representing a single standard deviation over the course of the program. Relative to the volume size distribution (Figure A.1), the number size distribution is shifted to the left and shows substantially greater variability. This is expected given that the formation of nanoparticles is very sensitive to small changes in dilution volume, temperature, etc. The number concentration variation will be affected by the cube of the mean number diameter of the aerosol. Thus, for example, a shift of ~8% in particle size will lead to a ~25% change in particle number concentration. As previously mentioned, the generation and monitoring protocol aimed to match mass concentrations across all exposure studies. The mass is dominated by particles on the right half of the plot, where

standard deviations are appropriately small. Figure A.6 compares average number size distributions between Phase 1 and Phase 2. It shows a tendency to higher particle number concentrations in Phase 2, consistent with the particle count results shown in main report Tables 4 and 5 and Figure 3. Figure A.7 compares average number size distributions across seasons. The differences appear to reflect chance variation, not true seasonal variation, in that summer and winter average distributions are nearly identical, while larger numbers of small particles are seen in the transition seasons. Figure A.8 presents the number size distribution for each exposure study.

Figure A.1: Average Volume Size Distribution throughout the course of the project. Error bars represent ± 1 standard deviation.

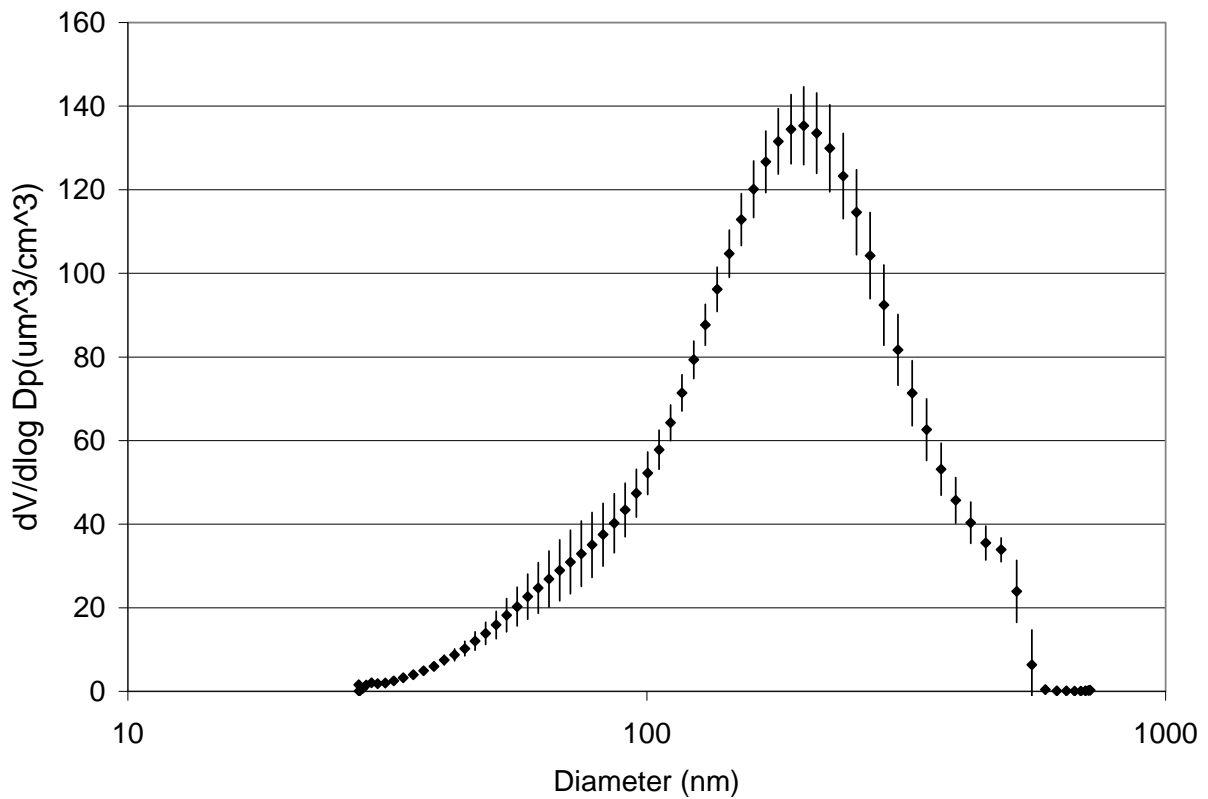


Figure A.2. Average volume size distributions in Phase 1 and Phase 2.

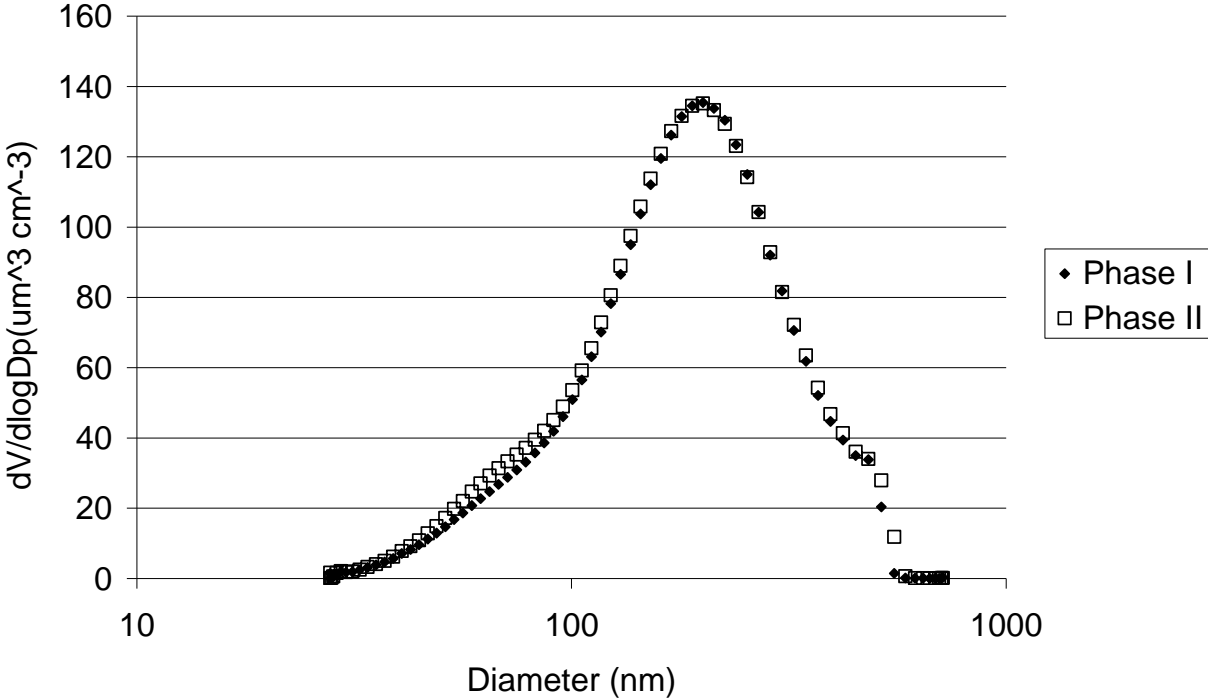


Figure A.3. Average volume size distributions by season, Phases 1 and 2 pooled.

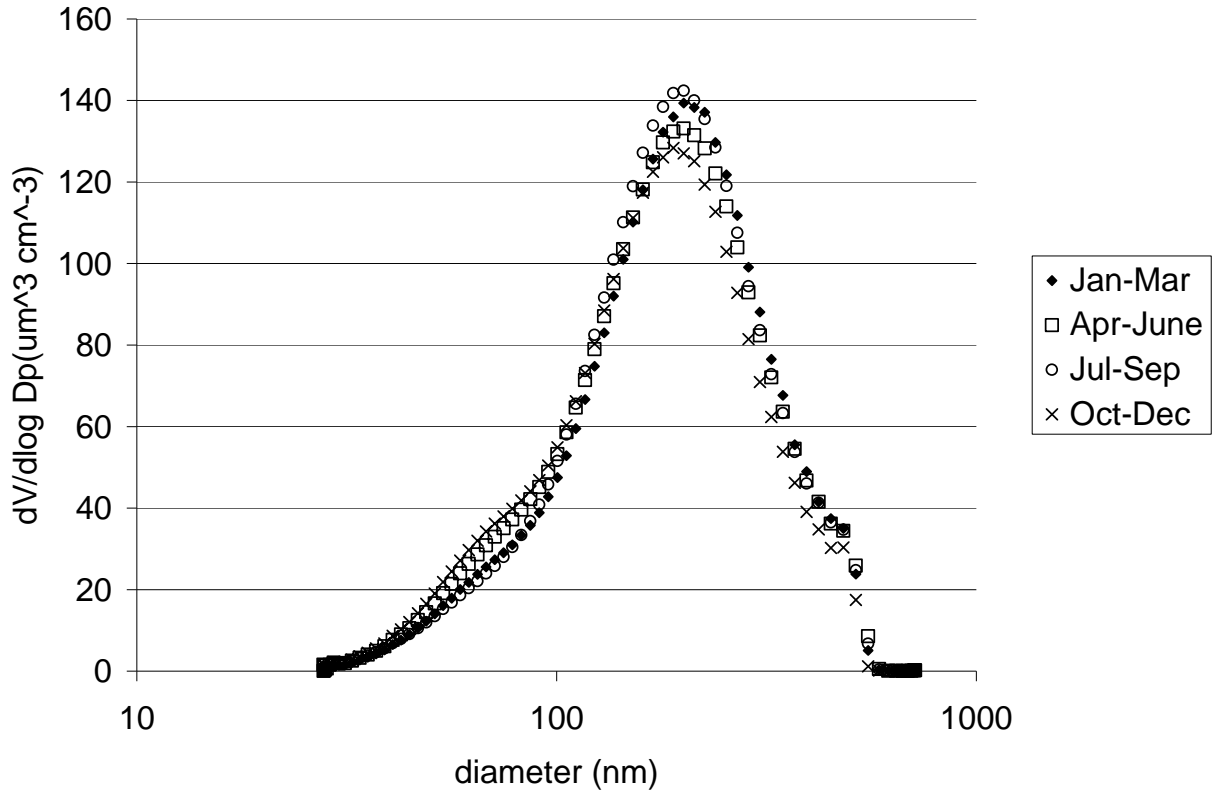


Figure A.4. Volume size distributions for each exposure study.

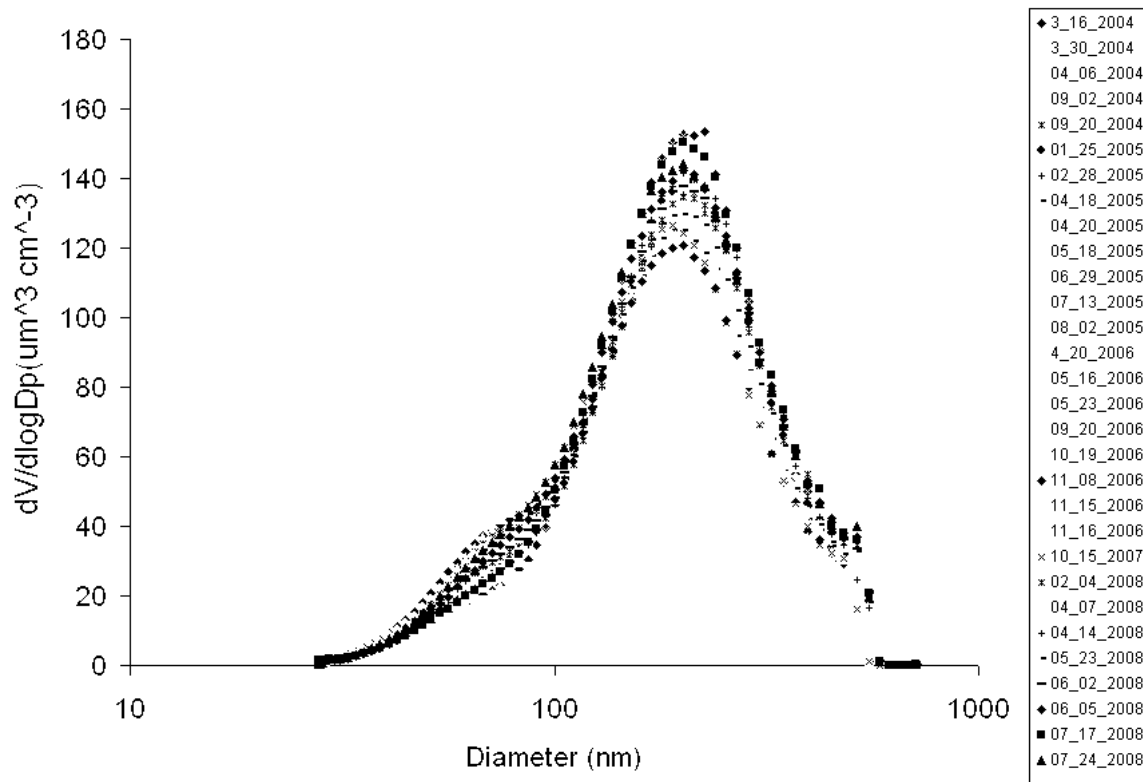


Figure A.5. Average Number Size Distribution throughout the course of the project.

Error bars represent ± 1 standard deviation.

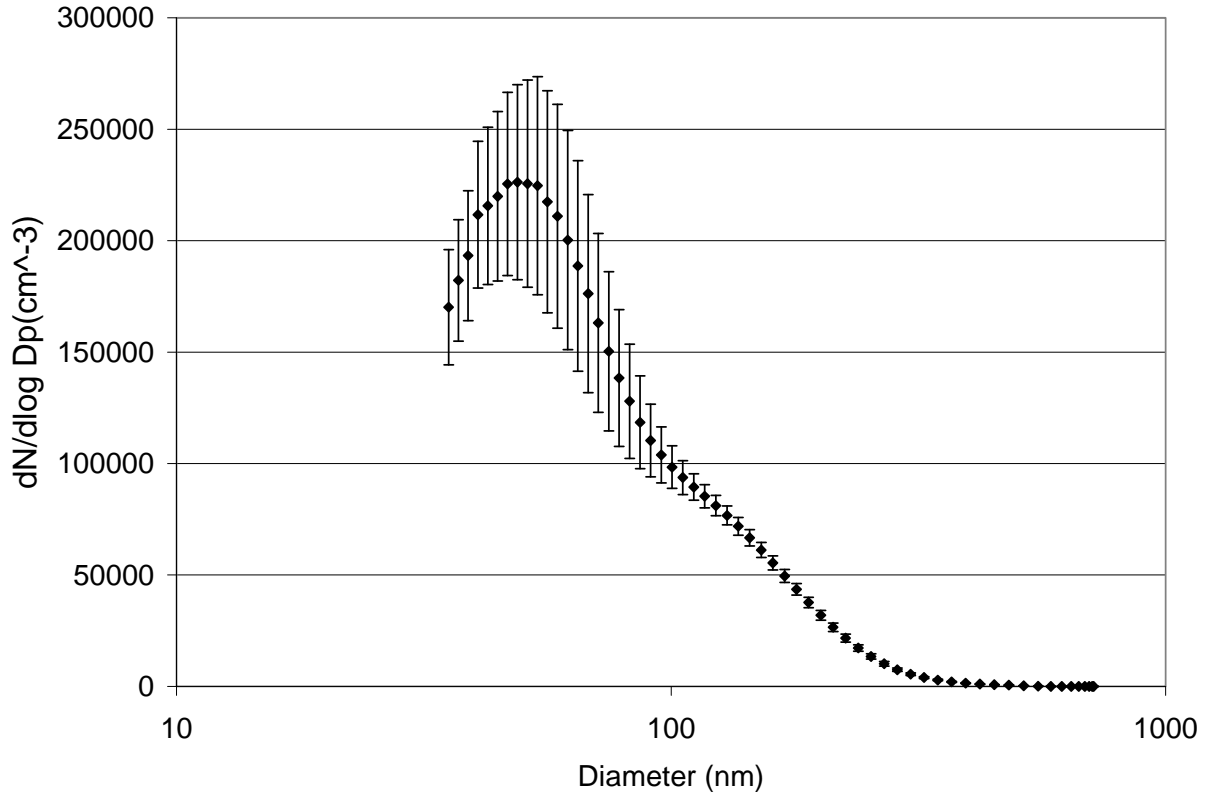


Figure A.6. Average number size distributions in Phase 1 and Phase 2.

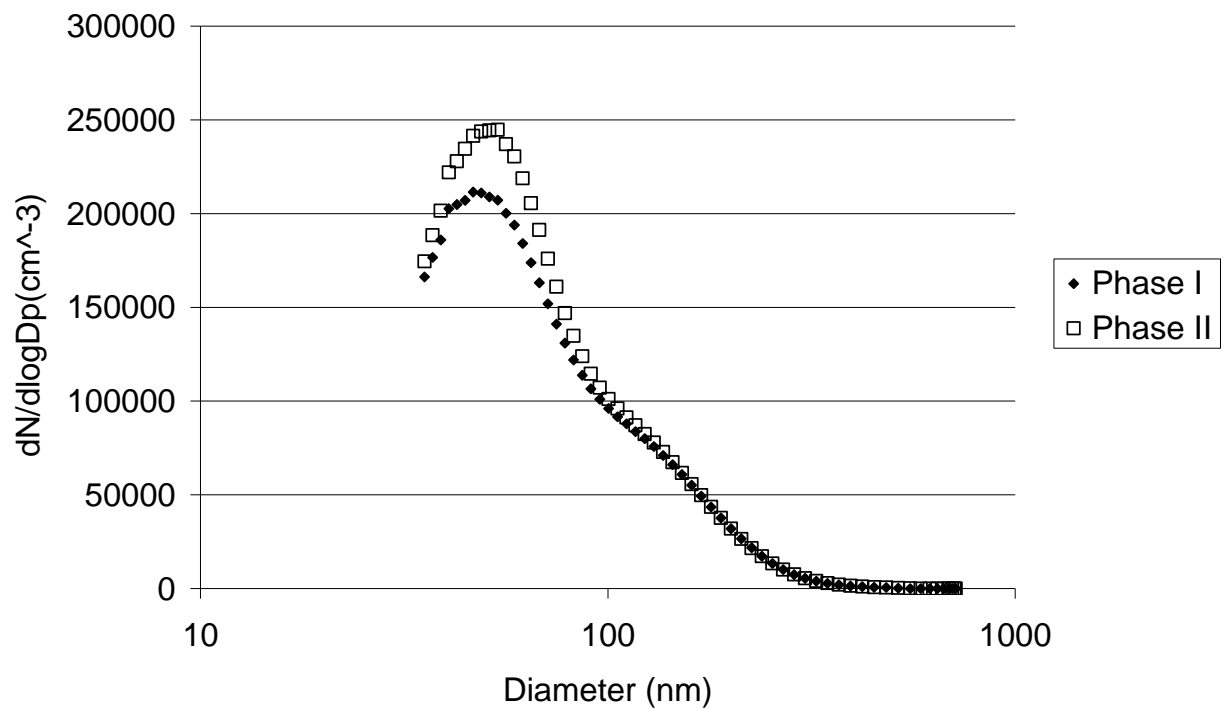


Figure A.7. Average number size distributions by season, Phases 1 and 2 pooled.

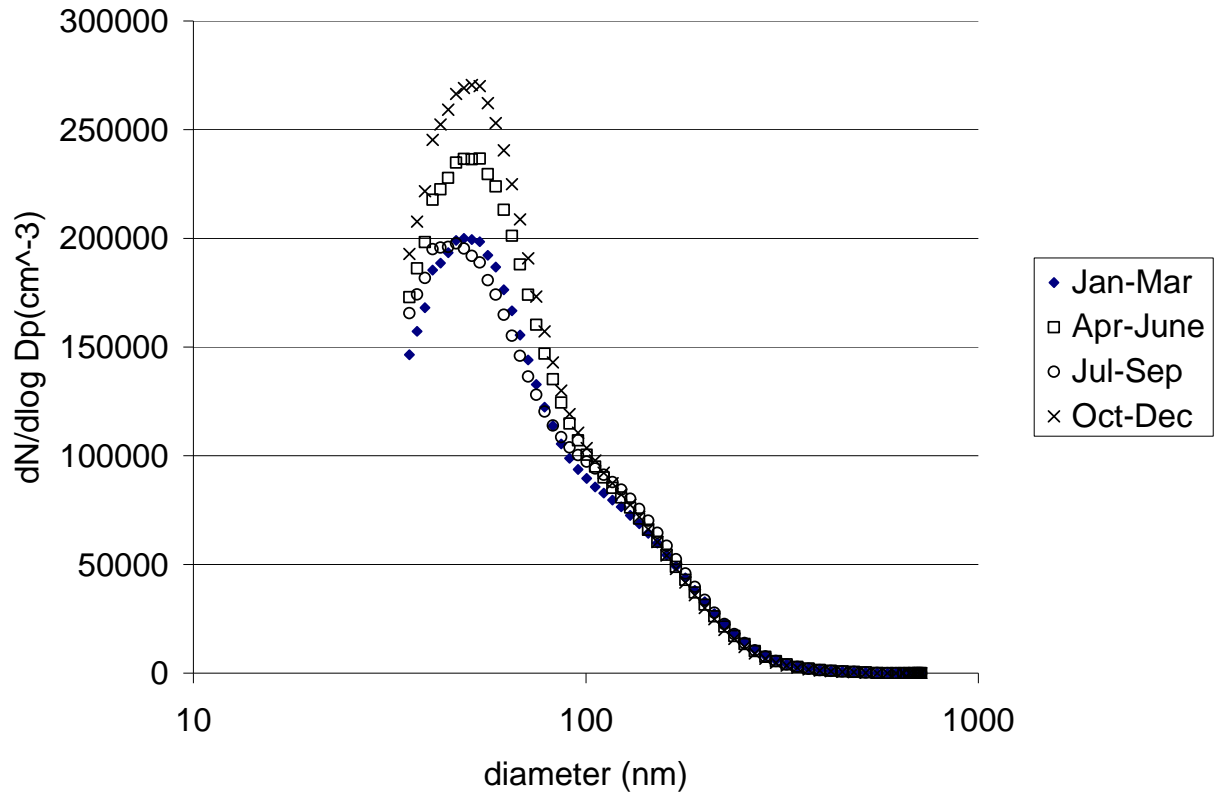


Figure A.8. Number size distributions for each exposure study.

